ASSESSMENT OF ORGANOTINS IN SEDIMENTS AND BIOTA COLLECTED FROM THE SAUDI COAST OF THE ARABIAN GULF

BY

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This thesis is dedicated to my late parents, may Allah forgive their sins, have Mercy on them and grant them al-Jannat ul Firdaus, amin

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LIST OF ABBREVIATIONS

OTC	-	Organotin Compounds
MBT	-	Monobutyltin
DBT	-	Dibutyltin
TBT	-	Tributyltin
MPhT	-	Monophenyltin
DPhT	-	Diphenyltin
TPhT	-	Tripheneyltin
DO	-	Dissolved Oxygen
TOC	-	Total Organic Carbon

ABSTRACT

Full Name : AKERE TAIWO HASSAN

Thesis Title : Assessment of Organotins in Sediments and Biota collected from the Saudi Coast of the Arabian Gulf

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Six species of organotin compounds were investigated in sediments and biota samples collected from Jubail, Khobar, Qatif and Half Moon Bay along the Saudi Coast Arabian Gulf. The relationship between total organotins, sampling locations, distances from the shoreline and physico-chemical parameters were assessed. The concentration ranges of MBT, MPhT, DBT and DPhT in sediment samples ranged from not detected to 345.2ng/g, 655.2ng/g,126.16ng/g and 673.3ng/g respectively. TBT and TPhT were below the detection limits in most of the sediment samples collected in this study. In the biota samples however, only TBT (3.4 – 12.92ng/g) and TPhT (14 – 39.9ng/g) were detected. Samples from Jubail harbour were significantly different from samples from the control location ($p<0.01$). There were no observed relationship between physico-chemical parameters and the concentrations of organotins. The distance from the shoreline was significantly related to the organotin concentrations. The organotin levels in samples from different locations showed variations and hence further detailed studies are required to assess the temporal and spatial trends.

KEYWORDS: - Organotin; Saudi Arabia; Sediments; Biota; Harbour

ملخص الرسالة

الاسم الكامل: أكيري تايو حسن

عنوان الرسالة: تقييم القصدير العضوي في الرواسب والكائنات الحية جمعت من ساحل السعودية على الخليج العربي

التخصص: العلوم البيئية

تاريخ الدرجة العلمية: مايو 2015

لقد تمت دراسة ستة أنواع من مركبات القصدير العضوي في الرسوبيات وعينات الكائنات الحية التي تم جمعها من الجبيل والخبر والقطيف وخليج نصف القمر على طول ساحل الخليج العربي السعودي. تم تقييم كلاً من العلاقة بين مجموع القصدير العضوي، ومواقع أخذ العينات، والمسافات من الشاطئ وكذلك العوامل الفيزيائية والكيميائية. تراوحت تراكيز MBT، MPhT، DBT وDPhT في عينات الرواسب من عدم الكشف الى 345.2 نانو جم/جم، 655.2 نانو جم/جم، 126.16 نانو جم/جم، و 673.3 نانو جم/جم على التوالي. كما كانت TBT وTPhT دون حدود الكشف في معظم عينات الرواسب التي تم جمعها في هذه الدراسة. اما في عينات الكائنات الحية فقد تم الكشف فقط عن TBT (3.4 - 12.92 نانو جم/جم) وTPhT (14 - 39.9 نانو جم/جم). وكانت عينات من ميناء الجبيل مختلفة إلى حد كبير من العينات من موقع التحكم (P <0.01). لم تكن هناك علاقة الملحوظة بين العوامل الفيزيائية والكيميائية وتراكيز القصدير العضوي. وكانت المسافة من الشاطئ ذات صلة إلى حد كبير بتراكيز القصدير العضوي. كما تباينت مستويات القصدير العضوي في عينات من مواقع مختلفة وبالتالي هناك حاجة ماسة لمزيد من الدراسات التفصيلية لتقييم الاتجاهات الزمنية والمكانية.

CHAPTER 1

INTRODUCTION

1.1 Background

Organotins compounds (OTC) are chemical compounds containing hydrocarbon and tin. The commonly encountered organotins compounds in the marine environment are monobutyltin (MBT), dibutyltin (DBT), tribuytltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT). They are used for various purposes in the industry: catalyst in chemical synthesis, heat stabilizers in PVC production, agrochemicals, industrial biocides and glass coatings (Okoro *et al.*, 2013; Sousa *et al*., 2013).

Tributyltin was commonly used as an active ingredient in marine antifouling paints to inhibit bio-encrustation. Antifouling paints or coatings hinder the growth of organisms that stick to the exterior of a ship or any submerged structure in water. Its efficacy results in its wide use in many commercial and non-essential vessels and crafts. When leached to the environment, organotin based antifouling paints are toxic to many marine organisms (Sousa et al., 2013). They cause endocrine disruption in gastropods resulting in the abnormal conditions such as imposex and chambering in Oysters (Cho, Lam, Lee, & Seol, 2014; Higuera-Ruiz & Elorza, 2011). It is noteworthy to state that not all organotins compounds have pesticide and biocide properties. Only triorganotins exhibit these properties. Mono and Di-organotins do not demonstrate these attributes.

The practice of using organotin based antifouling paints on small crafts or ships of less than 400 tons have been restricted or totally banned in many countries and regulated in large ships (Cho *et al*, 2014). These restrictions have not completely removed OC from the aquatic environment. They deposit to sediments after release and persist for a long time. Humans are at risk of exposure through ingestion of contaminated seafood. organotins compounds have been found in human samples (Sousa *et al*, 2013) and TBT is a known endocrine disruptors and immuno-suppressant (Okoro *et al*, 2013).

The international community recognizes the danger of organotin compounds to the environment. Initial restriction by many countries on the use of these compounds was followed by outright ban in 2008. Yet, many studies still report some elevated concentrations around the world. As these pollutants pose threat to the ecosystem and human health, monitoring is therefore necessary to fulfill legislative environmental directives and frameworks.

There has not been adequate documentation on the status of organotin in the Saudi waters. Very limited published information is available (deMora *et al*, 2003). There is no baseline information on the concentrations or distribution of organotins compounds in the marine environment along the Arabian Gulf coast of Saudi Arabia. There are also no environmental guidelines or regulations on the use and application of organotin based paints in marine vessels or offshore structures.

1.2 Problem Statement

The toxicological and ecotoxicological nature of organotins compounds makes it imperative to regularly monitor coastal waters for the level of pollution. With many offshore facilities, seaports and fish landing centres in Saudi Arabia, organotin pollution is expected to be present at significant concentrations. This is particularly disturbing because many oil vessels and cargo ships ply the Saudi waters and berth in the seaports on a daily basis. Hence, there is the need to know the current trend of organotins compounds distribution in the Saudi waters using latest sampling and analytical techniques.

1.3 Significance of Study

Coastal waters are being polluted with unregulated chemicals at an alarming rate. Some organotin compounds have been found to be highly toxic to marine species. The need for broad research on the level of concentration of these pollutants in the Saudi waters is therefore urgent in order to avert food and water poisoning crises in the near future, such as the case of Minamata disease in Japan. The outcome of this study will help the authority to better manage food and water resources through the adoption of stricter regulation on the use of chemicals and wastewater treatment techniques. It will also help to identify and suggest an environmentally safe limit for these compounds in seafoods.

1.4 Research Objectives

The main objective of this study is to assess the distribution and concentration of organotin compounds along the Gulf coast of Saudi Arabia.

The specific objectives are to study the:

a. distribution and concentration of organotin compounds in sediment samples collected from selected locations
b. level of organotins contamination in biota samples collected from selected locations
c. effect of environmental and water quality parameters on the concentration of organotin compounds in sediments and biota

CHAPTER 2

LITERATURE REVIEW

2.1 Organotin Compounds

Compounds that contain one bond at minimum between carbon and tin are referred to as organotin Compounds. They form bonds with organic groups such as alkyl or aryl and are grouped as mono-, di-, tri and tetra- compounds. The commercial use of organotins compounds revolve around five major applications: catalysts, biocides, heat stabilizers in PVC production (Sunday et al., 2012), agrochemicals (pesticides) and glass coating (Sousa et al., 2013). These applications of organotins compounds consume up to 20,000 tons of tin annually (Batt & Stewardship, 2006).

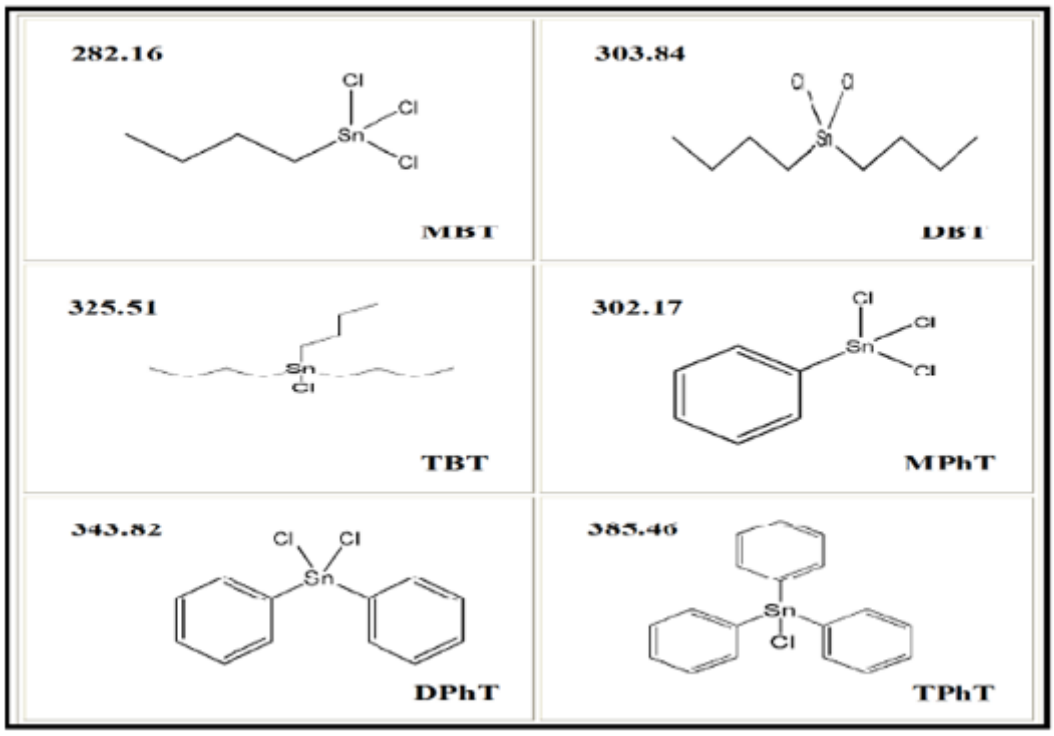


Figure 1: Molecular structures and molar masses of six species of organotin

2.2 Application of organotin Compounds

2.2.1 Applications of Mono and Di-organotin Compounds

Mono and di-organotins (MDO) are commonly used in the curing of coatings (electrocoat) and as catalyst in esterification and trans-esterification of polyesters. The final products are used in the production of polyester polyol, synthetic lubricants and plasticizers (Batt & Stewardship, 2006). These applications accounts for a large of use of MDO because they are few non-Tin based substitutes.

There is also a wide spread use of MDO as heat stabilizers in the production of polyvinyl chloride (PVC). In this process, organotins lower the degradation of the polymer backbone of the PVC by reacting with the HCl produced and making the unsteady chloride sites in the PVC molecule to be stable (Batt & Stewardship, 2006). The three main types of tin-based stabilizers are the methyltin, butyltin and octyltin stabilizers. In hot end coatings, MDO (predominantly as monobutyltin trichloride and dimethyl dichloride) are laid on the glass surfaces to prevent cracking.

2.2.2 Applications of Tri-organotin Compounds

Tributyltin (TBT), a member of the Tri-organotins (TO), is well known to exhibit biocidal properties. It is used in marine antifouling paints to repel the attachment of algae, barnacles etc (Okoro et al., 2013) from the underwater surface of ship's hull and structures submerged in water. This will increase the ship's fuel consumption efficiency, ship durability and prevent early dry docking. TBT was introduced in antifouling paints in the early 1970s to be freely dispersed as free association paint. The rate of leaching

was uncontrolled and very rapid (Thomaidis et al., 2007). As a result of the harmful environmental effect, a new technique was developed to incorporate TBT into copolymer paint formulation system. TBT was so effective that even small vessels and pleasure craft were coated with antifouling paint. The increasing usage made the environmental impact more significant.

TO are also used in agrichemicals as acaricides (to kill ticks and mites) and fungicides (de Castro et al., 2011). Triphenyltin Acetate and Triphenyltin hydroxide are used to kill fungi in order to protect crops when there is a high chance of a disease outbreak. Tricyclohexyltin Hydroxide, Tricyclohexyltin Triazole and Trineophenyltin Oxide are commonly used acaricides for citrus plants and vegetables.

2.3 Environmental Impacts of organotin

Many studies have reported the toxic nature of TBT based antifouling paints to marine organisms in all trophic level of the food chain, even at low concentrations. It was found out that Tributyltin induces a developmental disorder in marine gastropods called imposex (Axiak et al., 2000). Female dog whelks developed male sex organs (penis and vas deferens) (Evans et al., 2000). The oviduct is blocked by the growth of a penis, eventually becoming sterile and the females may die prematurely. The whole population can be negatively affected. Oysters exposed to continuous TBT had multiple chambers in the valves and shell abnormalities (Axiak et al., 2000; Higuera-Ruiz & Elorza, 2011).

The toxic effect of organotins compounds on mammals depends on the time of exposure, dose and the animal's physiological processes (Thomaidis et al., 2007). Studies on small laboratory animals show adverse effects on gastrointestinal tracts, growth, reproduction and central nervous systems (Okoro et al., 2013; Sunday et al., 2012). Humans exposed to organotins compounds may show eye and skin rash, and malfunctioning of the cardiovascular and gastrointestinal tracts (Abdulmumin *et al*, 2015).

These reported effects led to the ban of the use of TBT in many countries. France was the first, followed by many European countries, to ban the use of organotins compounds based paints on small vessels (Cho et al., 2014). The US passed the organotin Antifoulant Paint Control Act to restrict TBT based paints to craft larger than twenty five (25) meters in length. The International Maritime Organization also recommended a five-year plan to ban TBT paints worldwide beginning with a ban on its usage as of 1st, January 2003 and a complete ban on its occurrence on vessels as of 1st, January 2008. Despite the ban, many studies report elevated amount of organotins in various marinas and ports in the world. Many countries have set limits to the allowable concentration of organotin compounds in the environment.

2.4 Marine Environmental Monitoring of organotin

A variety of methodologies have been used for the separation and determination of organotins compounds. These methods can all be categorized into major groups: use of Gas Chromatography for the detection of organotin derivatives and the quantification of the mount of Tin present using Atomic Absorption Spectro-photometer (AAS).

Data for the monitoring of organotins compounds in marine environment of the Gulf region is very limited. The earliest available study done in the Gulf area was in Bahrain (Hasan & Juma, 1992) using AAS technique. They reported a TBT-Sn concentration of between 2.79 – 17.8 µg/1 in seawater with 5.97 µg/1 average and between 128 – 1930 ng/g in sediment with 732 ng/g average. This was at a time when the concentration of OC in sediments ranged from 30-670ng/g in Canada and USA (Hasan & Juma, 1992). The high values were attributed to an increasing use of TBT-based antifouling paints.

Stephen de Mora *et al* (2003) did another investigation of organotins in sediment and biota from four Gulf countries – Oman, Qatar, Bahrain and UAE (excluding Saudi Arabia). Here, the capillary Gas Chromatography with a flame photometric detector (HP 5890) was used. The study found that the sampled ROPME Sea areas had low concentration of organotin species except for few sample stations where the TBT concentrations in sediments were elevated, up to 60 ng Sng^{-1}. Low concentrations were recorded in most fish samples.

Organotins compounds have a wide distribution and have been reported in many marine environments across the world. Significant concentrations of organotins compounds in seawater, sediment and biota sample shave been reported in the coast of India (Bhosle et al., 2004), Greece (Thomaidis et al., 2007), Spain (Cassi, Tolosa, & de Mora, 2008; Higuera-Ruiz & Elorza, 2011), Venice lagoon in Italy (Berto et al., 2007), South Africa Harbour (Okoro et al., 2013), Suez Gulf in northeastern Egypt (Shreadah, 2011), South American coastal areas (de Castro et al., 2011) and even in Antartica (Negri et al, 2004).

CHAPTER 3

METHODOLOGY

3.1 Apparatus

The determination of the organotin compounds was performed on Agilent GC-MS 6890N System (gas chromatography - mass spectrometry). The GC-MS is fortified with Agilent 19091Z-213, capillary column (30m x 320 µm (ID) x 1µm film thickness), 6890B injector and an auto sampler 7683B series. Extraction of the organotin compounds was done using Accelerated solvent extractor. Water quality parameters (temperature, dissolved oxygen, pH and salinity) were measured by Eutech CyberScan PC 650Water Quality Monitoring instrument. A vortex mixer and a Lab Companion Shaker (model SK-600, GEOL Tech, Korea) were also used for thorough mixing. A Shimadzu TOC-V CPN analyzer was used in the determination of the total organic carbon in the samples.

3.2 Reagents and Standards

The standards used for the organotin compounds are shown in Table 1. They were purchased from Sigma-Aldrich, USA. A 1000 mg/ml solution was prepared in acetone and stored for dilutions when needed. Derivation of organotin compounds was done using Grignard reagent, methyl magnesium bromide. N-Hexane and dichloromethane were the solvents used. Anhydrous sodium sulfate was used for dehydration. They were also purchased from Sigma-Aldrich, USA.

Table 1: Standards for organotin Compounds

S/N	COMPOUNDS	STANDARDS	CAS No.
1.	Monobutyltin (MBT)	Monobutyltin trichloride	1118-46-3
2.	Dibutyltin (DBT)	Dibutyltin dichloride	683-18-1
3.	Tribuytltin (TBT)	Tributyltin chloride	1461-22-9
4.	Monophenyltin (MPhT)	Monophenyltin trichloride	1124-19-2
5.	Diphenyltin (DPhT)	Diphenyltin dichloride	1135-99-5
6.	Triphenyltin (TPhT)	Triphenyltin chloride	668-34-8

3.3 Study Area

The map of the study area is shown in Figure 2. The coordinates of the sampling stations are given in appendix A. The sampling stations include Jubail, Qatif, Khobar and Half Moon Bay (control). The selected locations are notable fish landing centers and have close proximity to offshore facilities, ship routes and seaports. Small and large cargo vessels and ships regularly ply the Saudi waters. It is thus expected that significant concentration of OTC used as antifouling paints will be found in these locations.

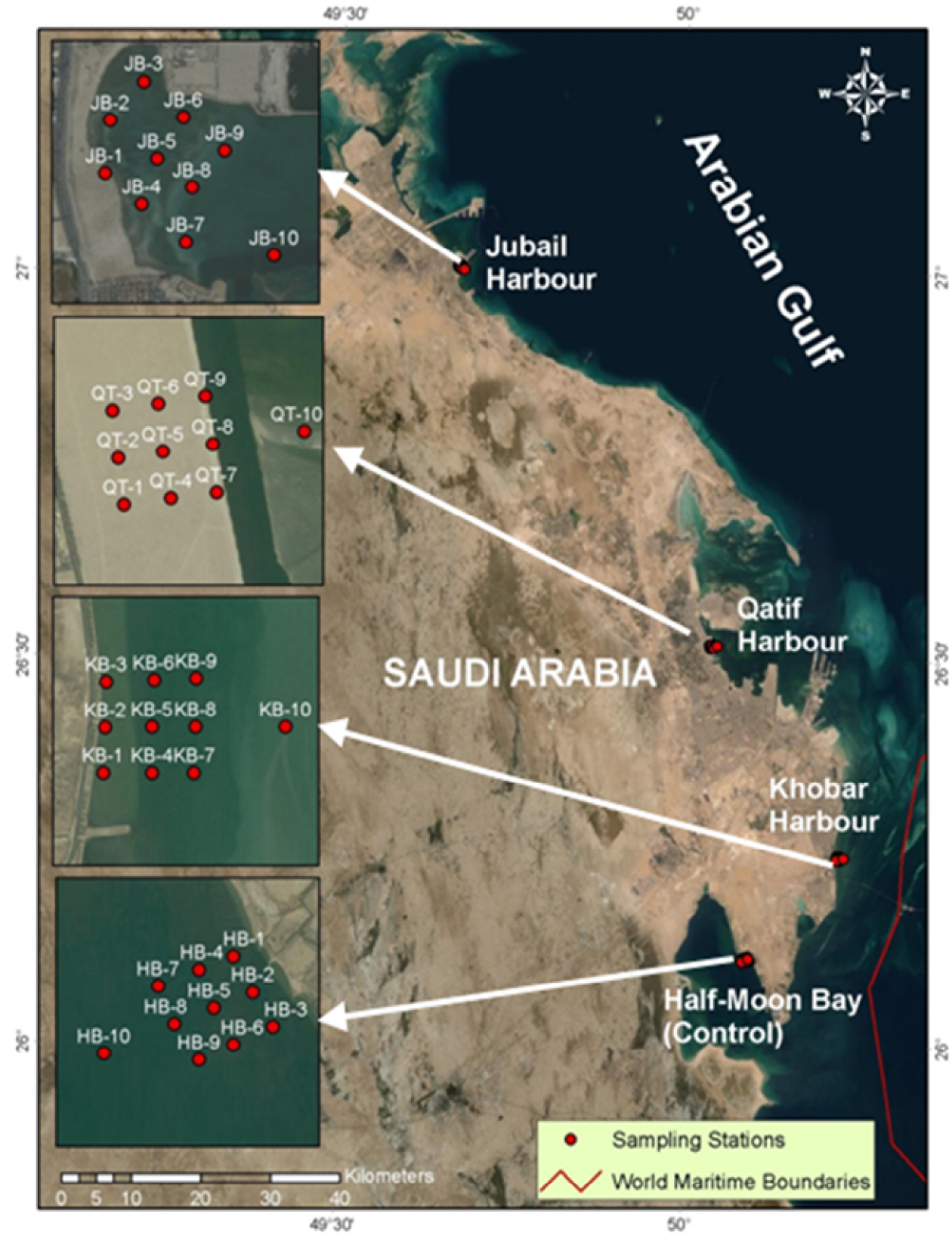


Figure 2: Sampling Stations

3.4 Sampling and Sample Preparation

3.4.1 Collection

Marine sediments and biota samples were collected according to US EPA Method 8323 (EPA, 2003). The sampling followed a predesigned sampling scheme to investigate the variation in sampling sites (Figure 3). Ten (10) stations were sampled in duplicates in each of the four sampling locations. Samples were collected 0m, 250m, 500m and 1000m from the shoreline. Approximately 2cm of top surface sediments were collected in honeycomb bottles using Van Veen Grab sampler attached to the research craft. In areas close to the shore and having low tide, sampling was done by scooping. The samples were stored under ice and transported at -18°C. They were then stored in freezer at the same temperature until analyses.

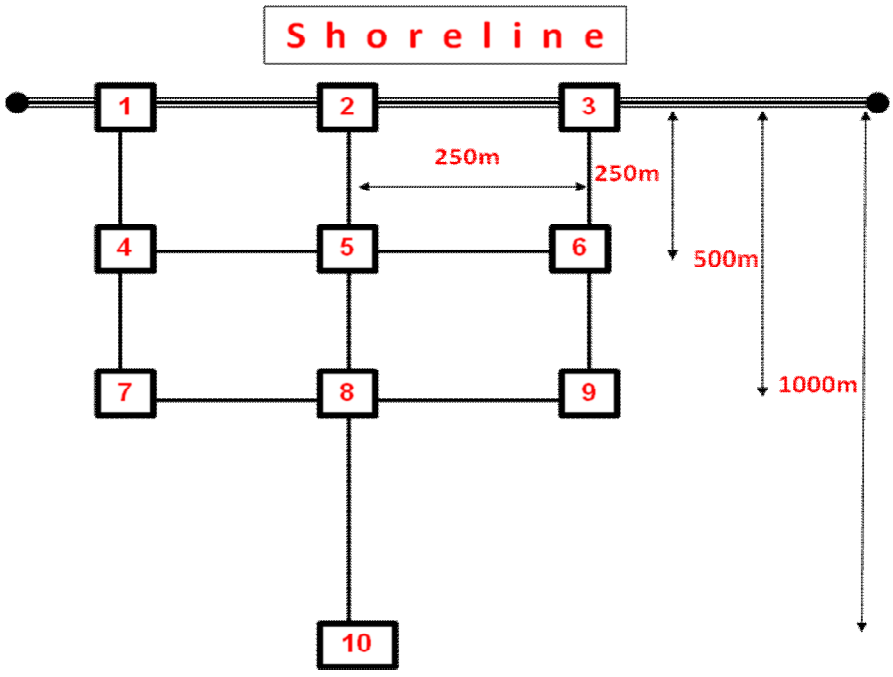


Figure 3: Sampling Scheme

Marine bivalves (*Meretrix meretrix* and *Chama species*) were collected from the Khobar and Qatif fishing harbors respectively. Biota (bivalves) samples were not found in the Jubail and Half Moon bay. The biota samples were collected by scuba diving and by hand picking during low tide (Appendix H). Immediately after collection, samples were transported under ice to the laboratory.

As part of efforts to gather information on the use of organotin based antifouling paints on ships berthing in the sampling areas, questionnaires (Appendix G) were prepared and distributed among stakeholders during sampling. The questionnaire requests information on the type of antifouling paints being used and the frequency of painting. At one of the sampling locations (Jubail harbour), painting of a large fish vessel with antifouling paints was witnessed (Appendix H). Photographs of the scene were taken and survey questionnaire was administered. The antifouling paint used, Wood and Wall Primer, was produced by the Saudi Paint Company, as a special purpose paints. Samples of the paint were also collected for analysis.

3.4.2 Preparation

3.4.2.1 Sediment Samples

The wet sediment samples were first air dried for analysis. About 200g of each sample were put in an aluminum foil and kept under fume hood at room temperature for about two days to dry out completely. Thereafter, the samples were ground to fine particle sizes

using mortar and pestle. A sieve was used to filter away silts and dirt. The fine samples were then transferred to labeled containers for extraction.

3.4.2.2 Biota Samples

The total weight and length of each bivalve was recorded (Appendix F). The biotas were grouped into three based on their relative sizes. This is to investigate the relationship between concentrations of organotins with biota size. From the Khobar harbour, AZ-01 is the smallest and AZ-03 is the biggest. From Qatif harbour, BZ-01 is the smallest and BZ-03 is the biggest. The biota samples were first allowed to thaw to ease preparation. They were then washed thoroughly with tap water. The valves were opened and the water content was drained. The tissues samples were carefully removed and freeze dried using Labconco FreeZone 2.5 freeze drier under high pressure and low temperature of -47°C. The dried tissues were ground to fine sizes with marble mortar and pestle, and weighed.

3.4.2.3 Antifouling Paint Samples

About 5ml of the paint sample were dissolved with 30ml of dichloromethane for 15mins and decanted to extract organotins. The digestion was repeated and decanted. The DCM layer was collected and pre-concentrated to 2ml under fume hood. 1ml of the concentrated extract was derivatized with about 500 µl of derivatization agent, methyl magnesium bromide for 20mins. The clean extract from the derivatization were separated out and analysed with GC-MS for quantitation. The result are presented in table x.

3.4.3 Extraction and Derivation of organotins

3.4.3.1 Sediment Samples

50mL of dichloromethane (DCM) was added to 5g of each sediment samples in a flask, stoppered and shaken for 30mins to effect extraction. Moisture contents were removed from the extract by addition of nips of anhydrous sodium sulfate. The extracts were then pre-concentrated to 1mL by heating in bath and by slow stream of dry liquid nitrogen. 1mL of n-hexane was added to 500µL of the pre-concentrated extract in a 5mL vial and agitated for 1 min. 500µL of the derivation reagent, methyl magnesium bromide, was then added to the extract. The whole mixture was shaken for another 1min. and kept at room temperature for 15min. 0.05 M Sulfuric acid was added to stop the reaction. The vial is then centrifuged and the upper layer was collected and analysed by GC-MS.

3.4.3.2 Biota Samples

Solid phase extraction method was used for the biota samples. 5g dry weight of the samples were minced, digested with 20 ml of deionized water by acetonitrile for 15mins and decanted. The digestion and decantation was repeated. The organotin compounds were extracted with 30 ml of n-hexane and rinsed with deionized water. The hexane layer was collected and the extraction technique was repeated once. The extracts were then transferred to a beaker and water residues were removed with anhydrous sodium sulfate. The extracts were evaporated and concentrated using rotary evaporator and stream of nitrogen. The concentrated organic extracts were derived with methyl magnesium bromide. Then the derived extracts were filtered out and the clean extracts were analysed for quantitation.

3.5 Determination of organotins

The separation and detection of the six organotin compounds were carried out using GC-MS 6890 System. The system is incorporated with an autosampler (7683B Series) and injector (6890B). The whole system is run by a Chemstation D.01.02.16, fitted with NIST 98.L library. The column used for separation was Agilent 19091Z-213 column of 50m x 320 μm x 1 μm film thickness of HP-1 methyl siloxane stationary phase. The carrier gas for injecting 1μL of sample volume was helium of elevated purity with a flow rate of 2.0ml min^{-1}. The temperature of the column was set to 40°C.

The calibration parameters for the sediment samples for the range of concentration of 0.05 – 10ng/g are shown in table 4. The limit of detection (LOD) and their respective limit of quantitation (LOQ) were calculated from the regression curve, using the slope and intercept values. A chromatogram was generated at the end of the operation showing the resolution of the different analytes. Figures 4-9 presents the ion chromatograms for the six organotin species. The mean percent recovery for the sediment matrix ranged from 80 – 94 %, and was estimated by spiking the respective samples with 0.01μg g^{-1} concentration. The retention time for the determination of the organotin standards at various concentrations (0.2, 0.5, 1, 2 and 5ppm) are shown in Table 3. The results were expressed as ng/g dry weight (ppb).

Table 2: Instrumentation Parameters for organotins Determination

Instrument	Agilent, 6890N system
Column	HP-1 column of 30m x320µm; 1µm methyl siloxane
He flow rate	2.0 ml min^{-1}
Acquisition mode	SCAN (50-550 amu)/SIM
Injection mode	Splitless
Injection volume	2µl
Oven temperature program	40°C (5 min) ramped at 12°C/min to 300°C (4 min)
Injection port temperature	250°C
MS Detector temperature	250°C
Interface temperature	250°C

Table 3: Concentration of organotin in Standard Solutions

organotin Compounds		MBT	MPhT	DBT	DPhT	TBT	TPhT
Retention Time (min)	**AveRT**	4.71	7.75	8.16	11.03	13.46	17.77
Conc. Std. ng/ml	**Ng**						
200	0.2000	271	263	584	948	617	520
500	0.5000	564	475	1178	1976	1287	1138
1000	1.0000	752	580	1518	2466	1699	1628
2000	2.0000	1735	1268	3422	5850	3966	3762
5000	5.0000	4139	2956	8152	14328	9674	9054
	Blank	4	-	3	1	1	6

Table 4: Calibration Parameters for Sediment Samples

Analytes	Slope	Intercept	R^2	LOD (ng/g)	LOQ (ng/g)	% Recovery
MBT	1269.1	422.4	0.994	1.0982	3.2946	94
MPhT	519.3	819.1	1.000	2.0927	6.2781	85
DBT	7052.2	1614.2	0.996	0.7553	2.2660	90
DPhT	3453.4	805.6	0.992	0.7698	2.3094	87
TBT	2485.7	848.7	0.991	1.1268	3.4145	82
TPhT	1709.5	213.2	0.992	0.4116	1.2473	80

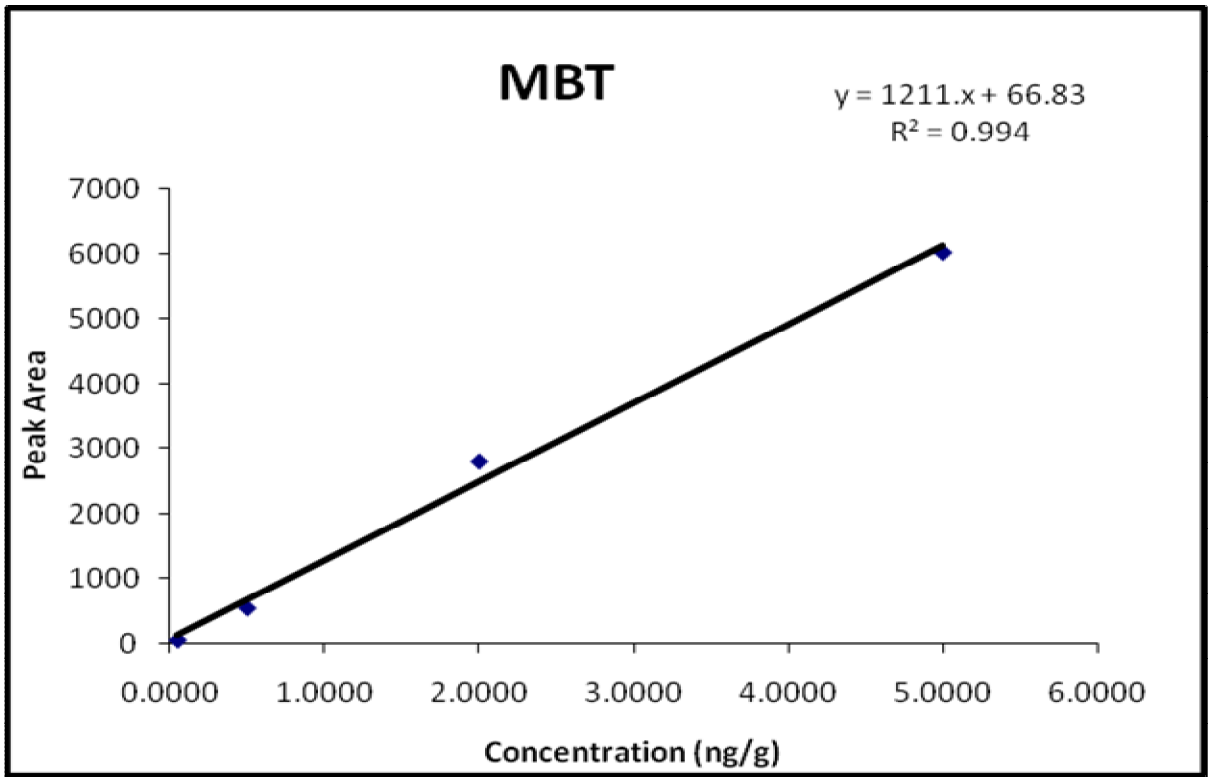


Figure 4: Calibration plot for MBT

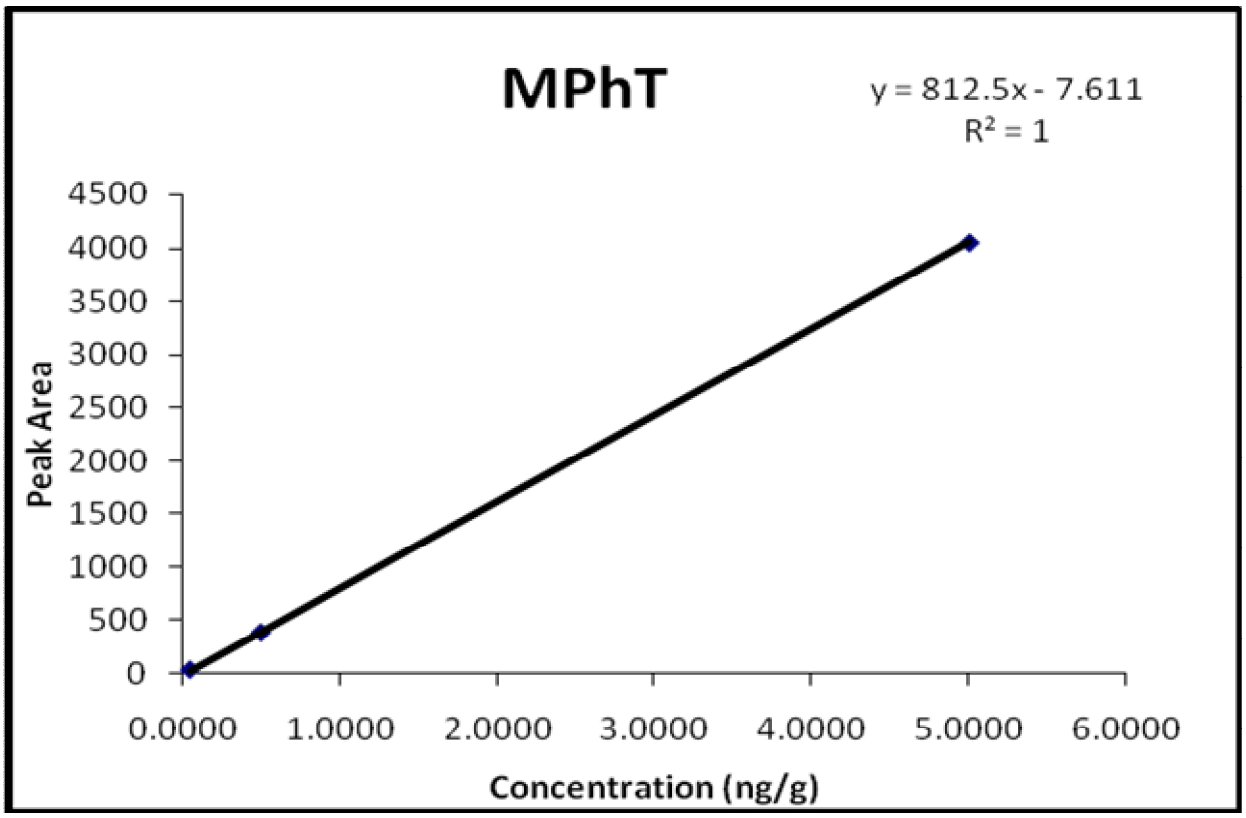


Figure 5: Calibration plot for MPhT

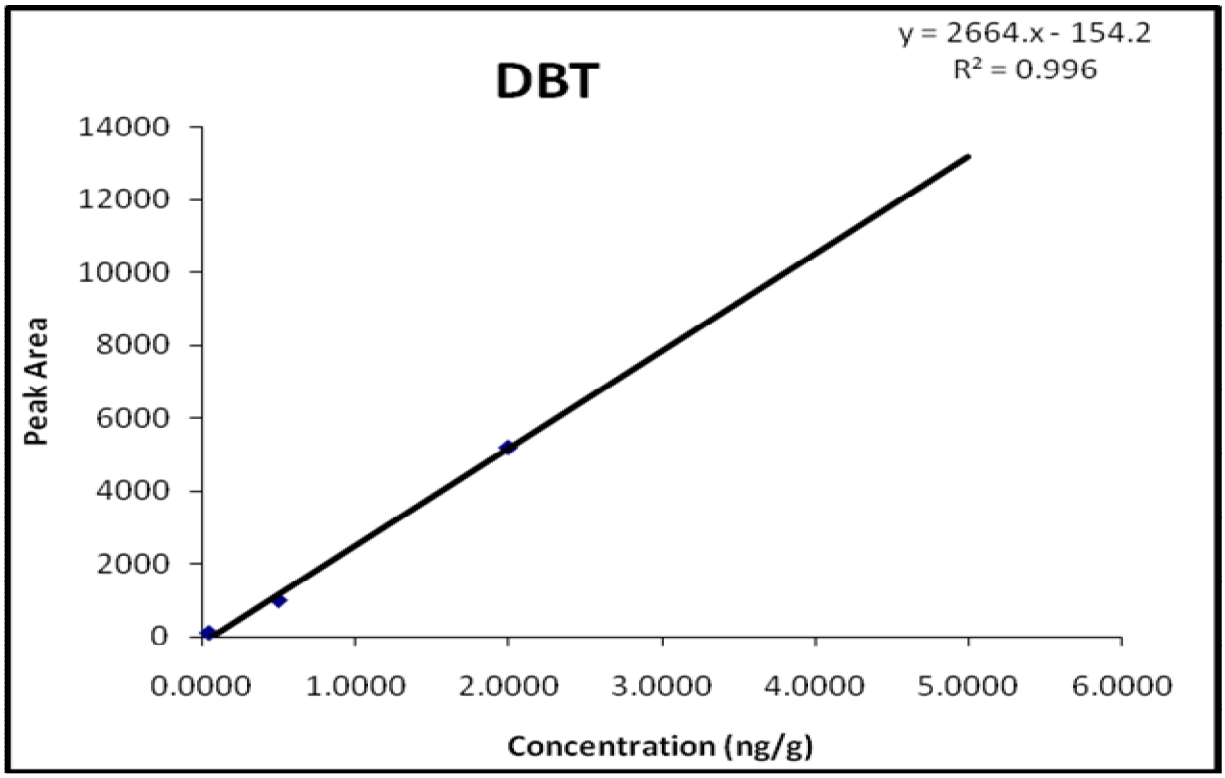


Figure 6: Calibration plot for DBT

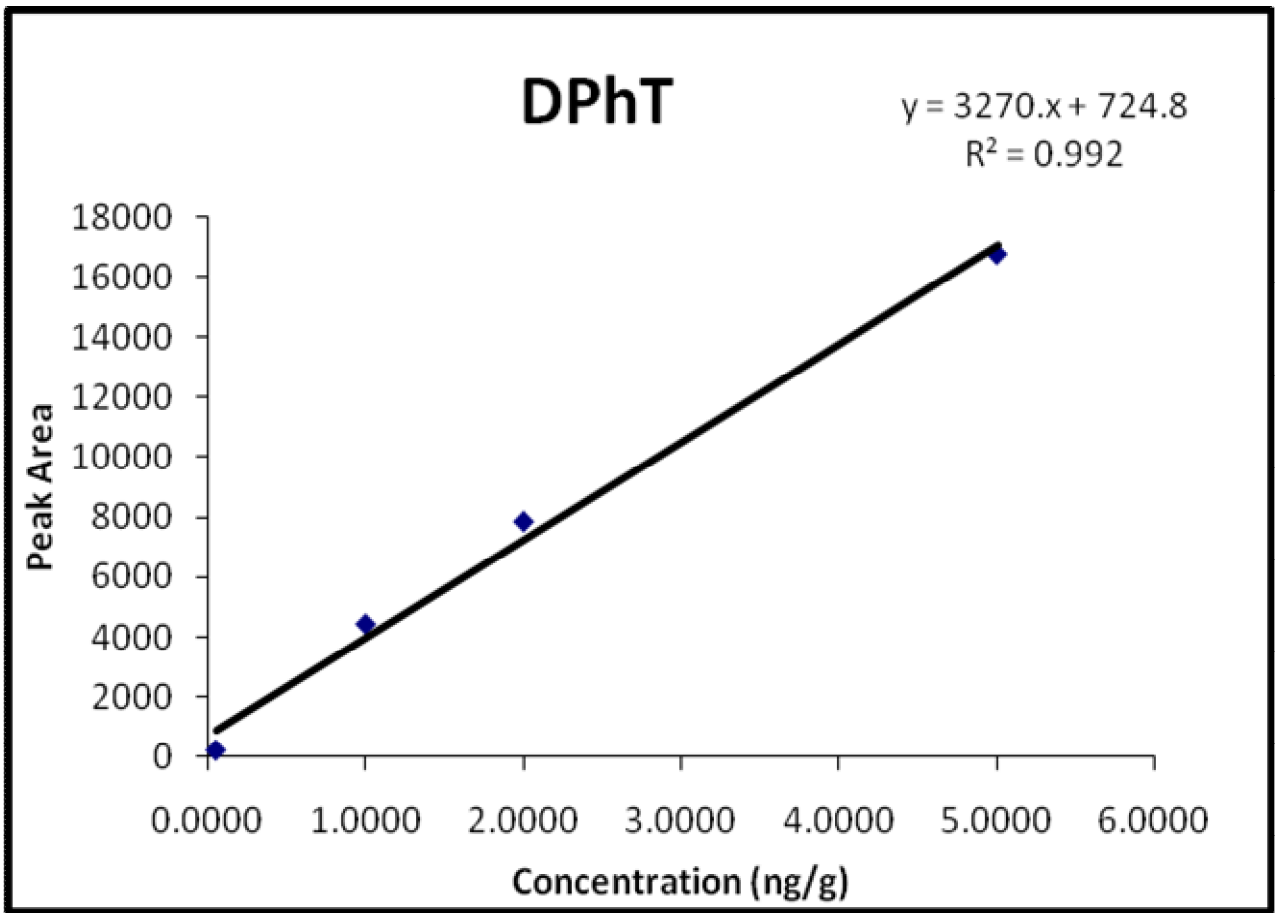


Figure 7: Calibration plot for DPhT

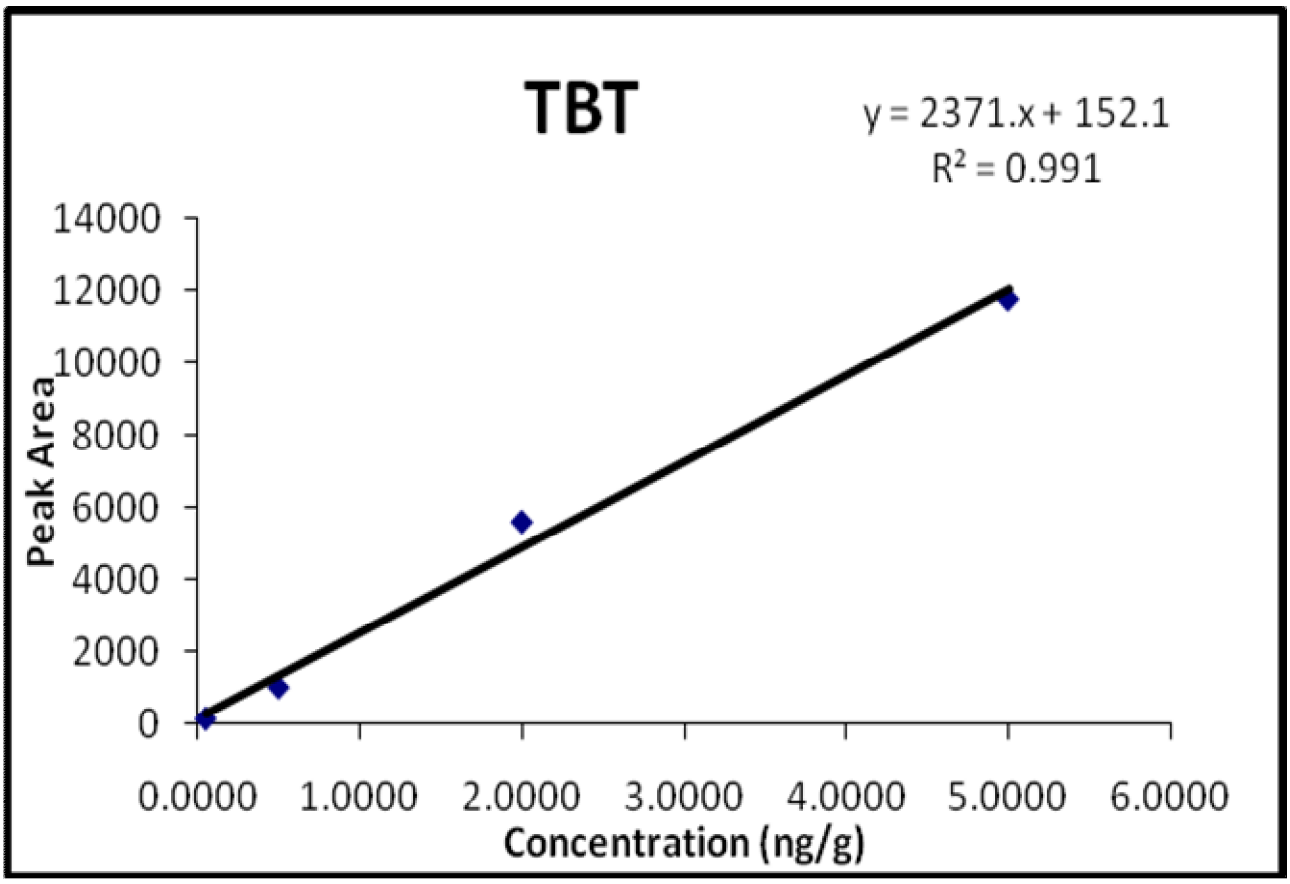


Figure 8: Calibration plot for TBT

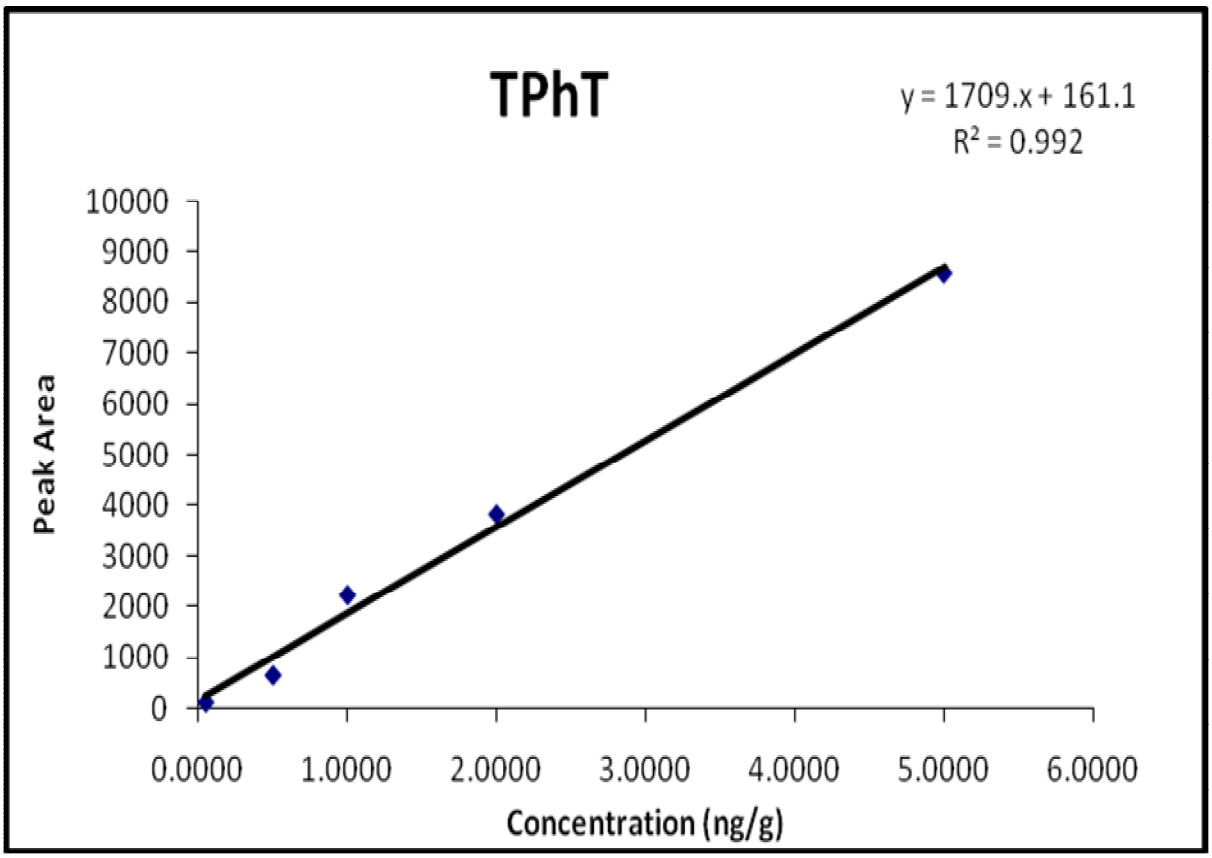


Figure 9: Calibration plot for TPhT

3.6 Environmental Quality Parameters

The following environmental quality parameters were measured *in situ* at each sampling stations: temperature, dissolved oxygen and pH. A handheld Eutech CyberScan PC 650Water Quality Monitoring instrument was used to measure these parameters. Salinity was measured using Atago Hand refractometer.

3.7 Grain Size Analysis

The analyses of the grain sizes were done using the well-established dry and wet sieving techniques (Poppe *et al*, 2000). About twenty (20) grams of each sediment samples were measured and rinsed carefully with distilled water on a sieve with mesh size of 63µm. The filtrates were poured into a sedimentation cylinder. 20ml of a dispersant, Sodium hexametaphosphate, was added to each tube and mixed thoroughly to effect the determination of the silt and clay fractions

3.8 Total Organic Carbon

The measurement of the total organic carbon (TOC) in sediment followed the standard EPA method 9060. All the samples and standard were weighed in ceramic boats. The TOC standard used is anhydrous dextrose. About 200mg of dried sediment samples were weighed in ceramic boats and labeled accordingly. They were treated with 0.4 – 0.5 ml of concentrated HCL to convert inorganic carbon in form of carbonates and bicarbonates to CO_2. The samples were then dried at 50°C and then placed in the solid sample module attachment designed specifically for the sediment samples. Each sample is combusted in

the TOC furnace and organic carbon in the sediment are converted to CO_2 and transported in carrier gas streams to be measured by an infrared detector.

3.9 Quality Assurance and Quality Control (QA/QC)

The QA/QC of organotin analysis and method validation was carried out using duplicate samples and spiking of standard solutions. Blanks were also included in all the analysis. The percentage recovery of the spiked sample solutions was used to determine the accuracy of the procedure.

3.10 Statistical Analyses

The results of this experiment were analysed statistically using R programming language and Microsoft Excel software, 2010 version. R is a programming language that is used for data analysis and statistical computing. Descriptive statistics was used to describe the distribution of the various organotin compounds among the sampling locations and stations. Normality test and test of homogeneity were done to ensure normal distribution. The differences in the mean concentration of the organotin compounds were assessed using Analysis of Variance (ANOVA). Gama regression was used since the data exhibited features of Gamma variables. Correlation and regression analysis were computed, and significance was determined at the 95% confidence level for all inferential statistical analyses.

CHAPTER 4

RESULTS AND DISCUSION

4.1 Determination of organotins in Sediments

The concentrations of the six species of organotin compounds under investigation in the sediment samples from each of the selected locations are presented in appendix B. The average concentration of the six organotin species found in the sediment samples is 423.89±331.3ng/g, as summarized in table 5. The highest concentration (673.3ng/g) was recorded in Jubail fishing harbour while the least concentration (nd - not detected) was recorded in all locations.

In total, the phenyltins were more in abundance in sediments than the butyltins from the sampled locations. The highest amount of MPhT (1086.40ng/g) was found in samples from Jubail harbour and the lowest amount was from Half Moon Bay (8.00ng/g), the average being 382.53±243.17ng/g. It is worth noting that, individually, MPhT was the most abundant (1530.10±243.17ng/g) of all the six organotin species in the sampled locations. This was closely followed by DPhT, with a total concentration of 1409.44±345.23ng/g. DPhT was not found at all in Qatif harbour and Half Moon Bay. Average DPhT concentrations of 138.79±70.04ng/g and 2.15±2.15ng/g were found in Jubail and Khobar harbour respectively. TPhT was below detection limits in all sampling locations except in one station in Jubail (34.60ng/g)

With a total concentration of 595.88±121.55ng/g, MBT was the most abundant of the butylated form of organotin under investigation. It was found in all locations except Half Moon Bay. The highest concentration of MBT found in a sample (344.00ng/g) was

recorded in Jubail harbour while the lowest concentration (2.39ng/g) was recorded in Khobar harbour, the average being 148.97±121.55ng/g. DBT was found in all four locations with a total concentration of 385.78±153.37ng/g and average of 96.45±76.68ng/g. Jubail harbour recorded the highest concentration of DBT (125.58ng/g) while Half Moon Bay recorded the lowest (1.00ng/g). TBT was below the detection limits in all four sampling locations.

In general, sediment samples from Jubail, Khobar and Qatif harbours are significant difference from the control location (p<0.05). Sediments from Jubail harbour had the highest concentration of the organotin compounds (Figure 10). This is very much expected considering the high volume of industrial and agricultural discharges, as evidenced by the elevated amount of total organic carbon from the area (Table 23 - 26). Being one of the largest fishing harbours in the Eastern province, and the various industrial activities in Jubail may account for the elevated amount of organotins. High concentration in this harbour could also be linked to the extensive use of organotin based antifouling paints on large fishing vessel. Only at this harbour were the ship repairing and painting observed..

Significant difference (p<0.05) between the distance from the shoreline and organotin concentrations were observed. Most of the organotins recorded were from stations that are within 0 - 250m from the shoreline. With distance from the shoreline, there was an exponential decrease in the concentrations of organotin at all locations (Figure 11). This is most likely due to the ship berthing and repair activities that are usually done at the shore area. In a similar study, Hasan *et ali* (1992) observed that there was a decrease in organotin concentration away from the origin.

The reason for the low concentrations of TBT and TPhT in the samples from the study area may be due to their unstable nature. These compounds usually undergo photolysis in the presence of UV radiation and breakdown into their respective lower molecular species which are more stable. In addition, the fact that most of the sampled areas have fine sands/coarse silts and shallow depths enhances degradation of these compounds (Filipkowska *et* al, 2011). This accounts for the high concentration of MBT, DBT, MPhT and DPhT in the sediment samples. Elevated amount of the lower molecular organotin species could also be a result of recent inputs of organotins originating from other sources such as industrial wastewaters and sewage effluents. This is corroborated by the exceptionally high amount of these compounds in the paint samples retrieved from the Jubail harbour (table 6).

In a similar study in China where Wang *et al* (2008) investigated six species of organotins, only the lower molecular organotins species were detected. This was attributed to inputs from industry effluents and urban sewage. In the neighbouring Bahrain, Hasan & Juma (1992) reported an elevated average concentration of TBT (732ng/g) in sediment samples. In the Suez canal, Shreadah *et al* (2011) attributed the high organotin concentrations (Average: TBT – 1300ng/g, TPhT – 1100ng/g) to shipping events in the harbour and industrial discharges. Yet, a higher concentration of total organotins (19,180ng/g) was reported by Filipkowska *et* al (2011) in the Gulf of Gdansk in northern Europe. According to the Australian environmental quality guidelines of 5ng/g for TBT in sediments, most of the sediment samples from Jubail, Khobar and Qatif exceeded the limits and poses hazard to benthic organisms close to the harbour.

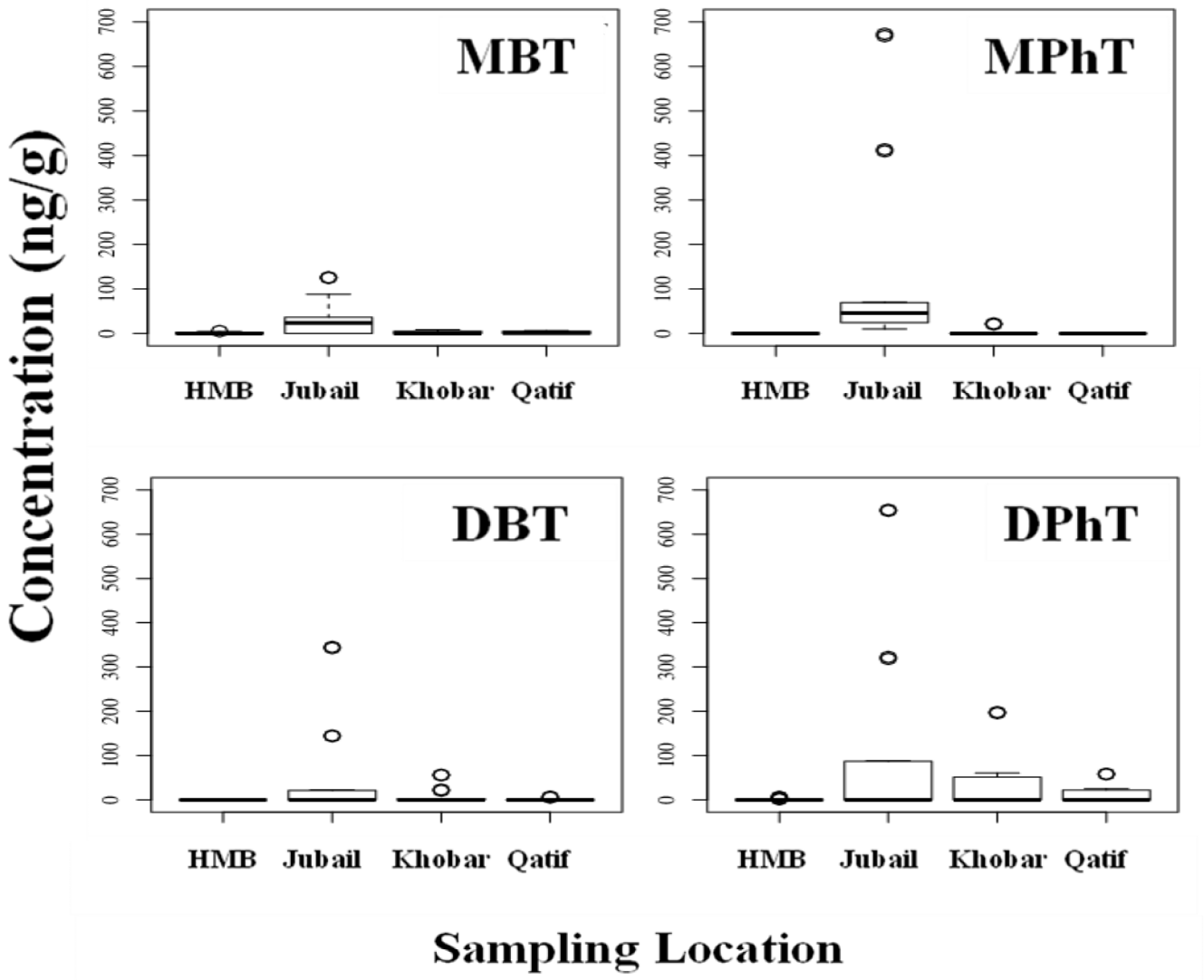


Figure 10: Total Concentration of organotins in Sediments

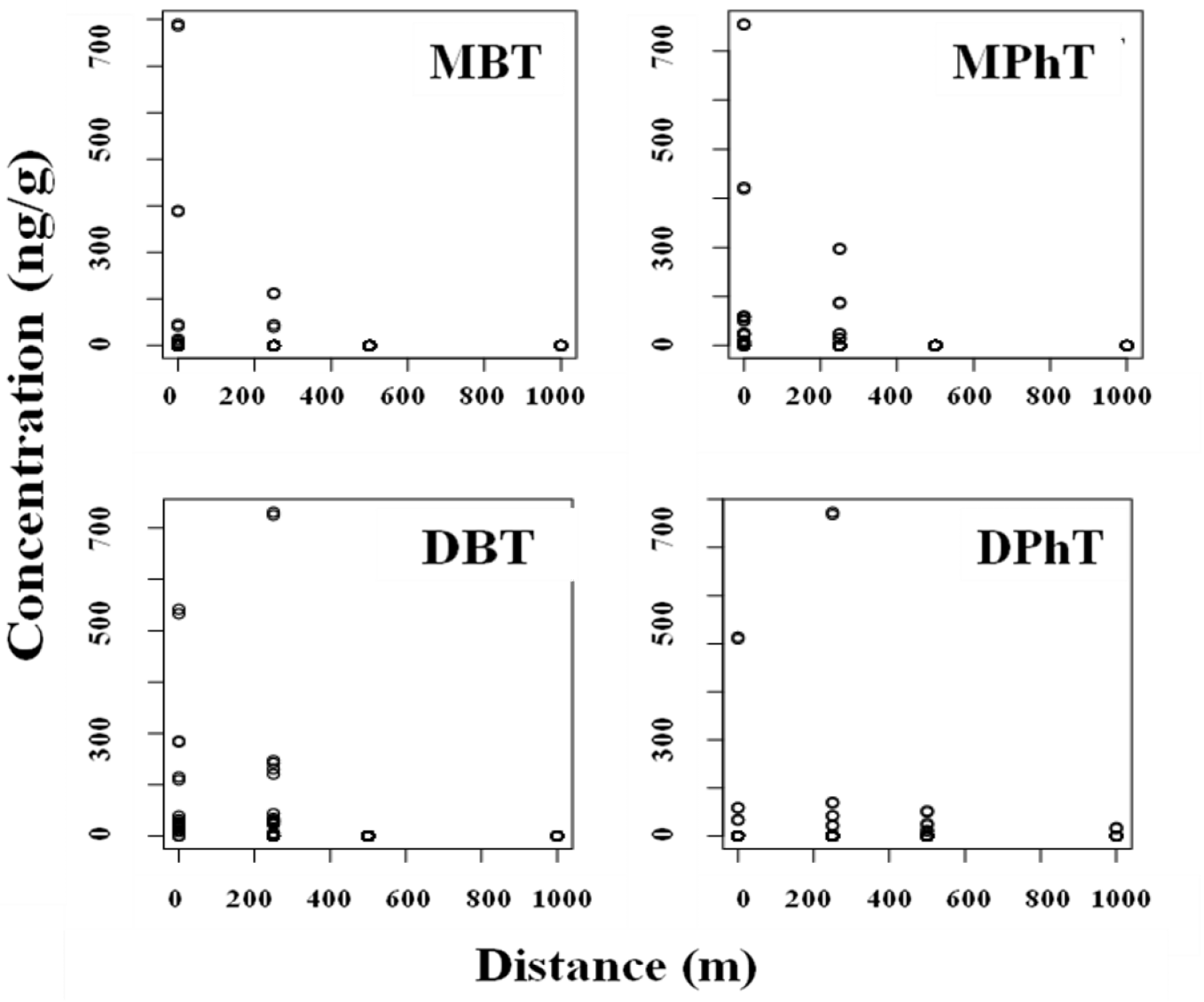


Figure 11: Distribution of organotins in Sediments with distance

Table 5: Average Concentrations of Organotin in sediments

Location	MBT	MPhT	DBT	DPhT	TBT	TPhT	MEAN (ng/g)
Jubail	50.95±112.39	108.64±216.16	32.64±42.31	138.79±221.5	nd	3.46±3.46	334.48±434.49
Khobar	8.03±18.19	31.7±62.38	2.36±3.2	2.15±6.8	nd	nd	44.24±89.16
Qatif	0.61±1.93	11.87±19.01	2.39±2.65	nd	nd	nd	14.87±21.95
Half Moon Bay	nd	0.8±1.93	1.2±1.87	nd	nd	nd	2.0±3.23

Table 6: Concentration of organotins in Antifouling Paint Sample

Sample ID	MBT	MPhT	DBT	DPhT	TBT	TPhT	MEAN (ng/g)
Paint Sample	0	228,554	399,277	40,442	0	0	668,273.00
						Average	111,378.83
						SD	166,651.22

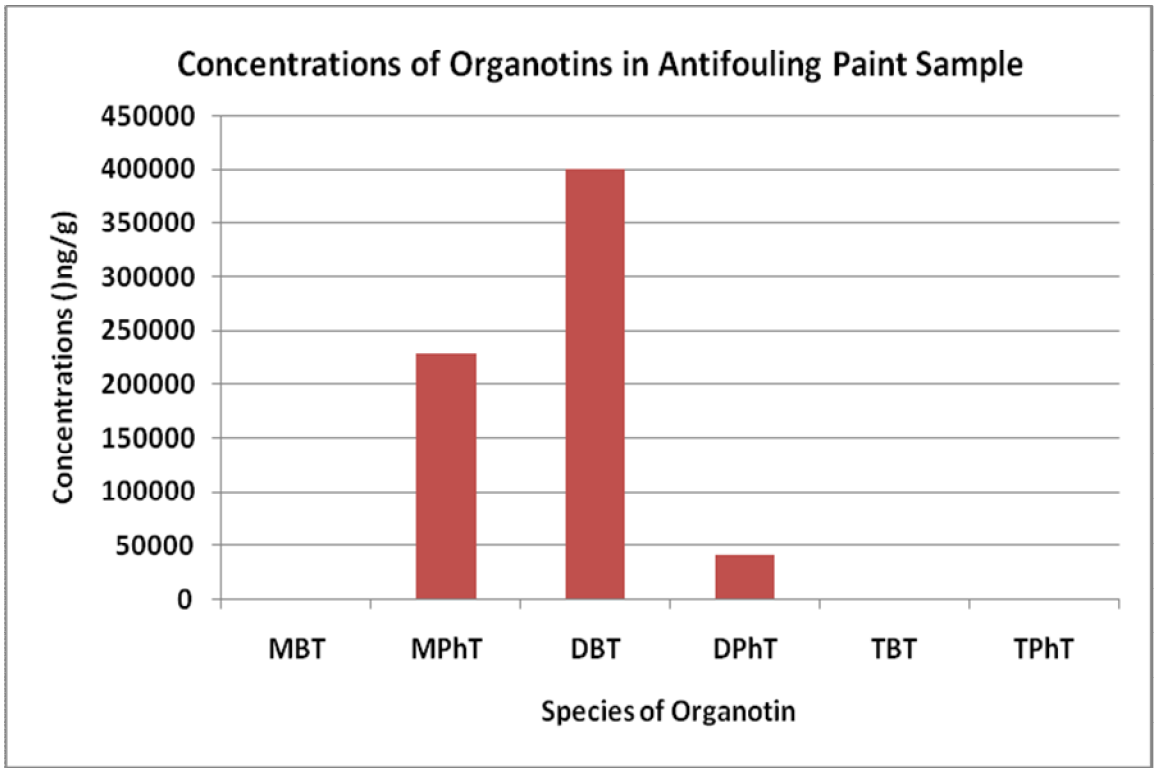


Figure 12: Concentration of organotins in Antifouling Paint Sample

4.2 Determination of organotins in Biota samples

The concentration of organotins found in the biota samples are shown in Table 7 and the distributions are presented in Figures 13 and 14. TBT and TPhT were the only organotin species found in the biota. MBT, MPhT, DBT and DPhT were below the detection limits. Generally, TPhT concentrations were higher than TBT in all the sampled locations. The total concentration of organotins in biota sample was 172.87±10.48ng/g. The total TPhT concentration from Khobar harbour was 60.20±5.66ng/g (Average = 20.07±3.27ng/g) while for Qatif harbour was 72.40±13.66ng/g (Average = 24.13±7.88ng/g). The total TBT concentration from Khobar harbour was 22.65±4.73ng/g (Average = 7.55±2.73ng/g) while for Qatif harbour was 17.62±3.32ng/g (Average = 5.87±1.92ng/g). The concentrations of TBT and TPhT were highest in the largest biotas (AZ -03 and BZ-03).

Figure 15 and 16 compares the concentrations of the six organotins species in sediment and biota from Khobar and Qatif harbour respectively. The species of organotin found in the biota samples were in direct contrast to the sediment samples. TBT and TPhT that were not detected in the sediment samples are the only organotin species found in the biota. This suggests an absence or low degradation in the biota tissues compared to sediment samples. The result of this study is similar to what Hugo *et al* (2008) reported from San Vicente Bay in Chile. In that study, butyltins were investigated in bivalves and only TBT was detected. The high abundance of TBT in biota samples reported from the west coast of India was attributed to slow degradation and new inputs of TBT from antifouling paint leaching (Bhosle *et al*, 2004).

Table 7: Total Concentration of organotins in Biota samples

	Sample ID	MBT	MPhT	DBT	DPhT	TBT	TPhT	TOTAL (ng/g)
Khobar Harbour	AZ-01	nd	nd	nd	nd	4.00	14.00	18±5.62
	AZ-02	nd	nd	nd	nd	5.73	21.00	26.73±8.42
	AZ-03	nd	nd	nd	nd	12.92	25.20	38.12±10.58
Qatif Harbour	BZ-01	nd	nd	nd	nd	3.40	16.00	19.4±6.4
	BZ-02	nd	nd	nd	nd	4.57	39.90	44.47±16.02
	BZ-03	nd	nd	nd	nd	9.65	16.50	26.15±7.09

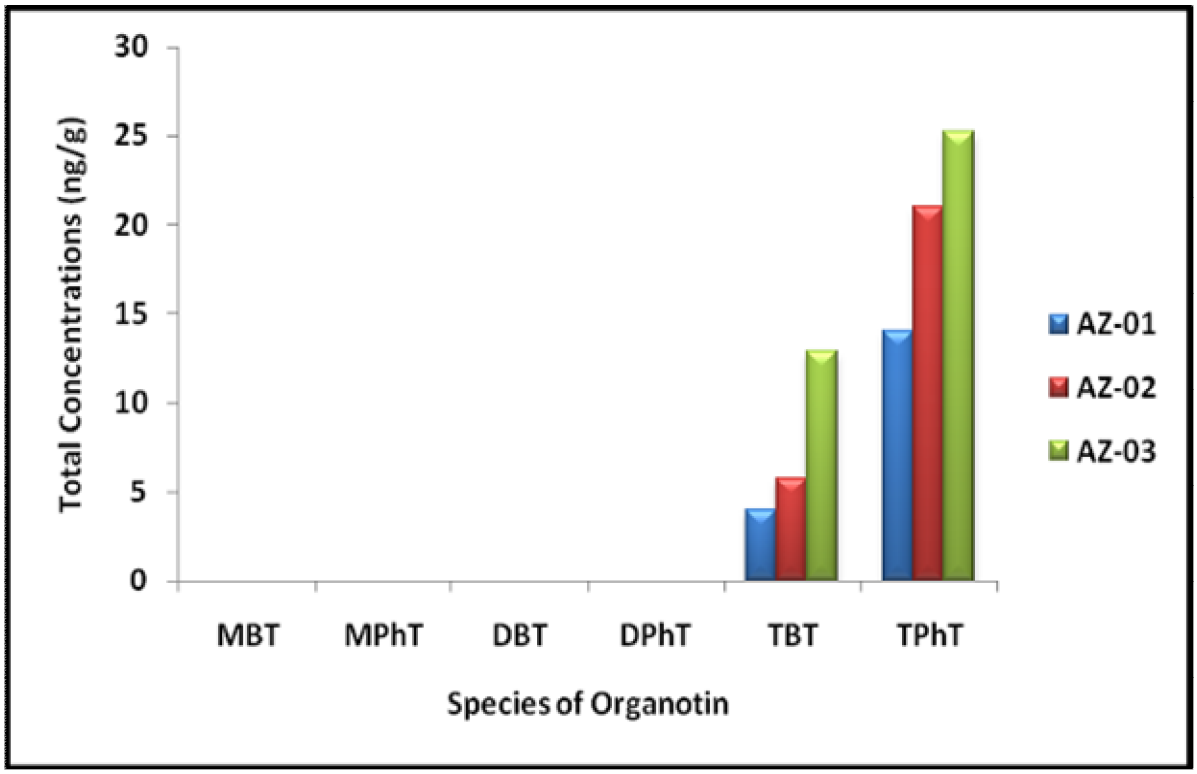


Figure 13: Concentration of organotins in Biota samples of different size groups from Khobar Harbour

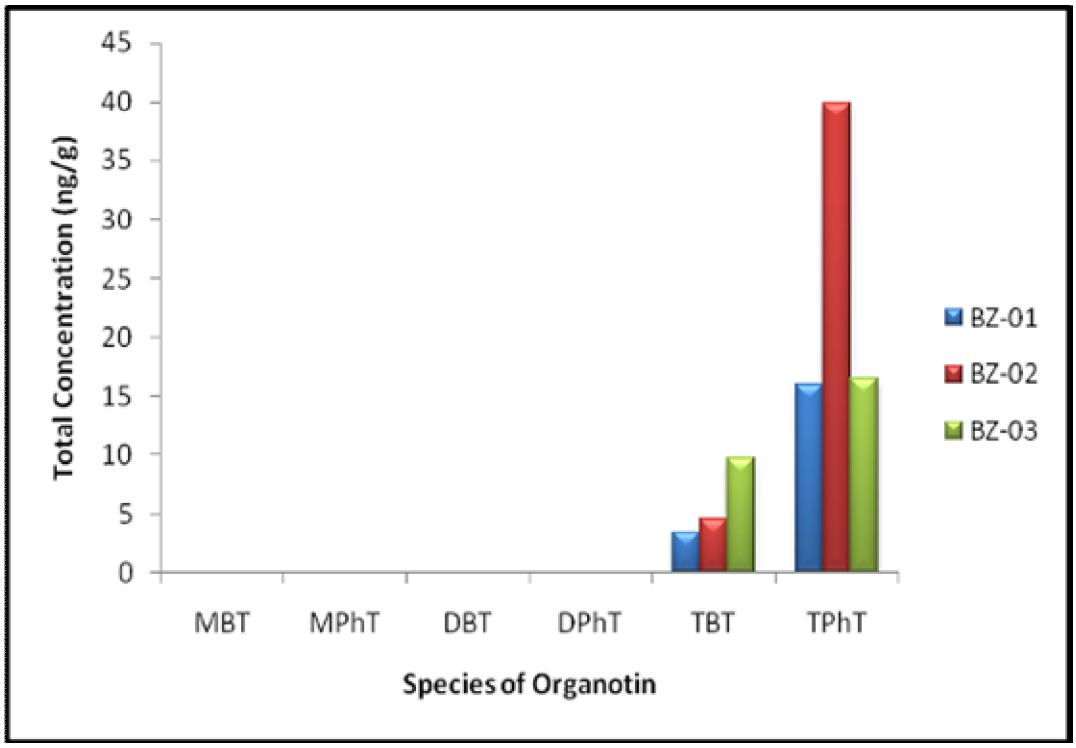


Figure 14: Concentration of organotins in Biota samples of different size groups from Qatif Harbour

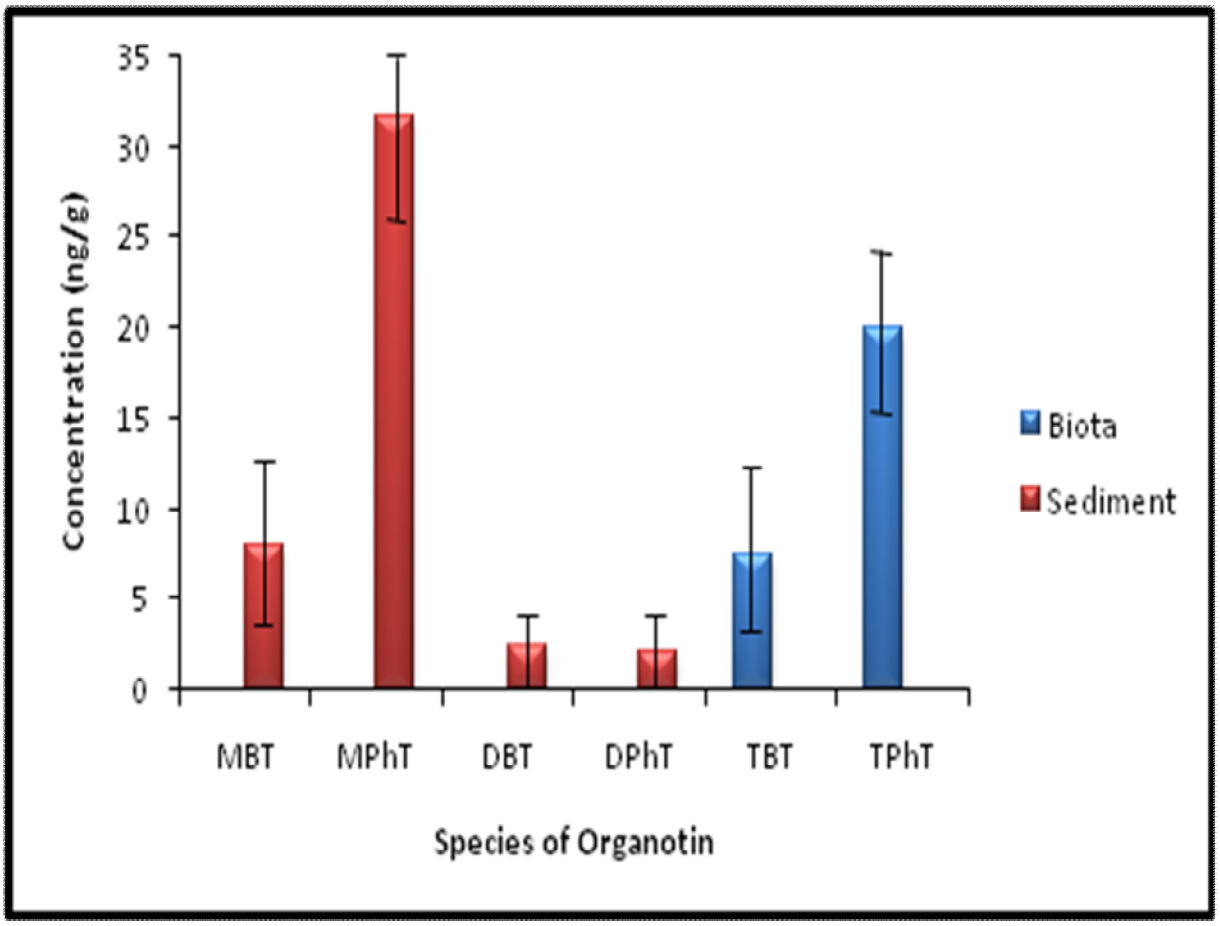


Figure 15: Comparison between average concentration of organotins in Sediment and Biota from Khobar harbour

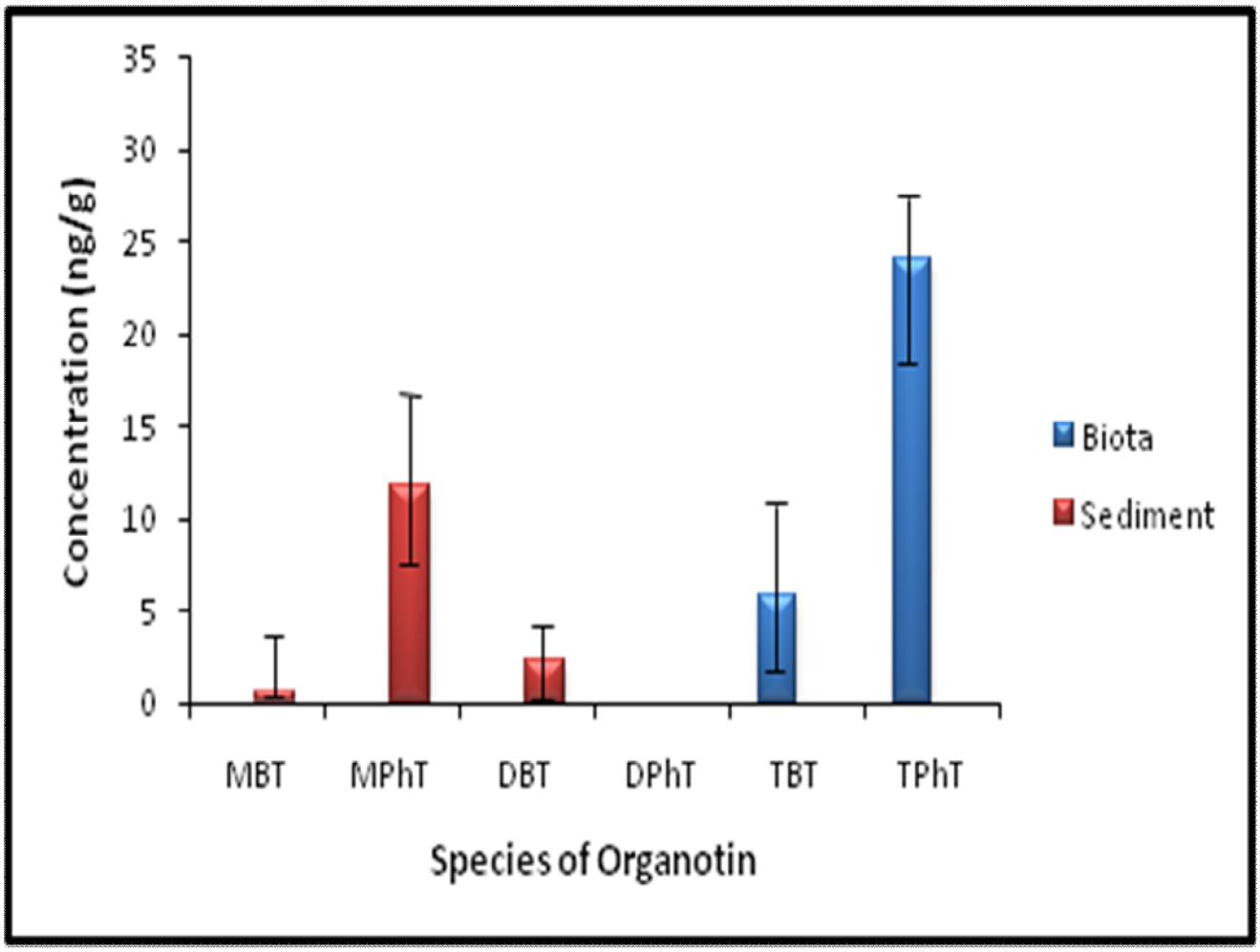


Figure 16: Comparison between average concentration of organotins in Sediment and Biota from Qatif harbour

4.3 Effect of Environmental Quality Parameters

Table 8 shows the average values of the water quality parameters from all sampling locations. The temperature ranged between 20 - 22°C in all stations. The pH value ranged from 7.19 – 8.05. Khobar harbour recorded the highest salinity of 46.6±2.12 while the lowest value was in Qatif (36.4±2.01). The temperature, pH and salinity results do not show any observed relationship with the organotin concentrations in the sample locations. While the organotin concentrations vary widely among the locations, the values of these parameters have narrow variations. The grain size analyses revealed that most of the sampled locations have coarse silt and fine grained sand (Appendix E). Hoch (2004) and Filipkowska (2011) opined that organotin are likely to bind to fine grain sizes with high TOC content.

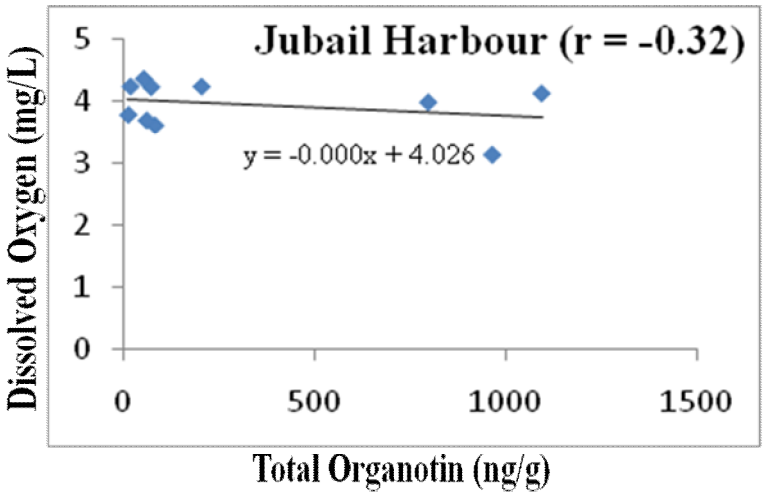
Figure 17 shows the correlation analysis between dissolved oxygen and organotins concentrations in sediments from all sampling locations. Half Moon Bay was not compared because most of the organotin concentrations were below detection limit. Jubail and Qatif harbours have negative correlations ($r = -0.32$ and $r = -0.27$) respectively, while Khobar harbour shows no correlation. There is a wide variation in the correlation analyses.

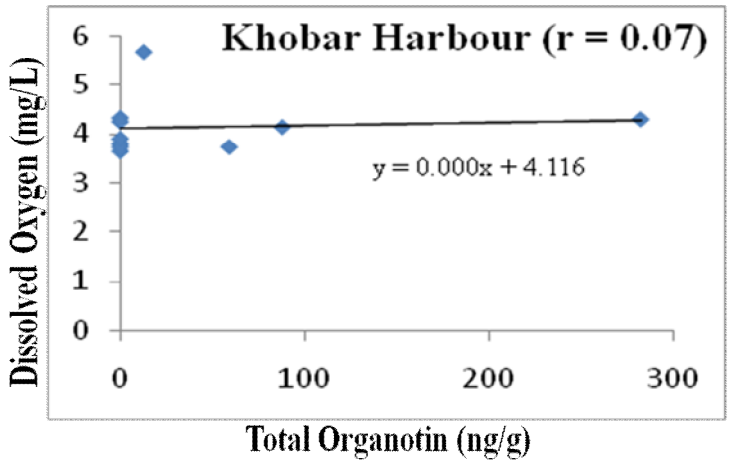
The concentrations of total organic carbon in sediments from all locations are presented in appendix D. Figure 18 shows the correlation analyses between total organic carbon and organotins concentrations. Jubail harbour has a moderate positive correlation ($r = 0.65$), Khobar harbour has a negative correlation ($r = -0.20$) and Qatif harbour has a weak positive correlation ($r = 0.31$). No observed relationship can be established from these analyses, corresponding to what Filipkowska *et* al (2011) reported in Poland.

Table 8: Average Water Quality Parameters for all locations

(Mean ± standard deviation)

Location	Temp. (°C)	pH	Salinity (ppt)	DO (mg/L)	TOC (ng/g)
Half Moon Bay	21.73±0.39	7.19±0.19	36.8±1.48	7.02±0.26	4.99±0.38
Jubail	22.93±0.25	7.37±0.03	41±2.58	3.93±0.38	141.11±8.31
Qatif	20.85±0.17	7.93±0.23	36.4±2.01	5.05±0.56	194.07±8.71
Khobar	22.95±0.2	8.05±0.26	46.6±2.12	4.14±0.6	235.79±34.84





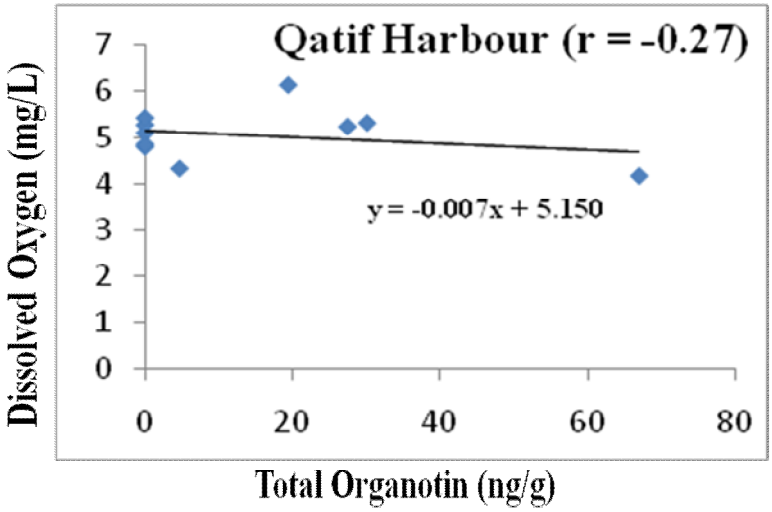
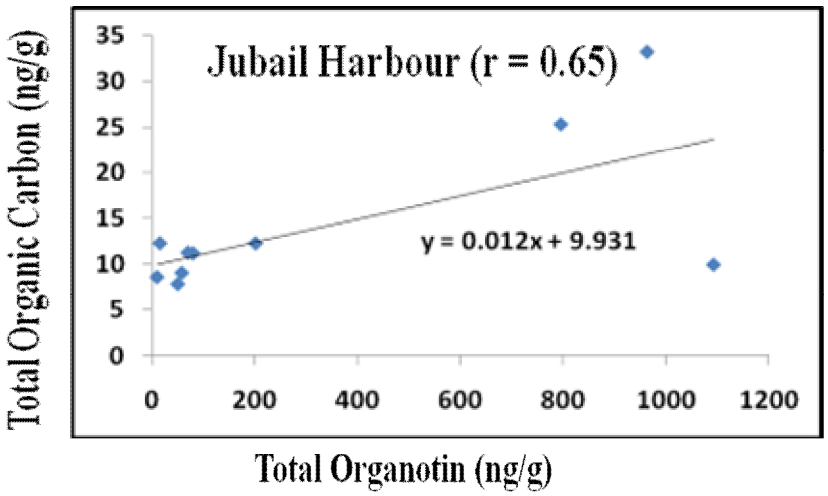
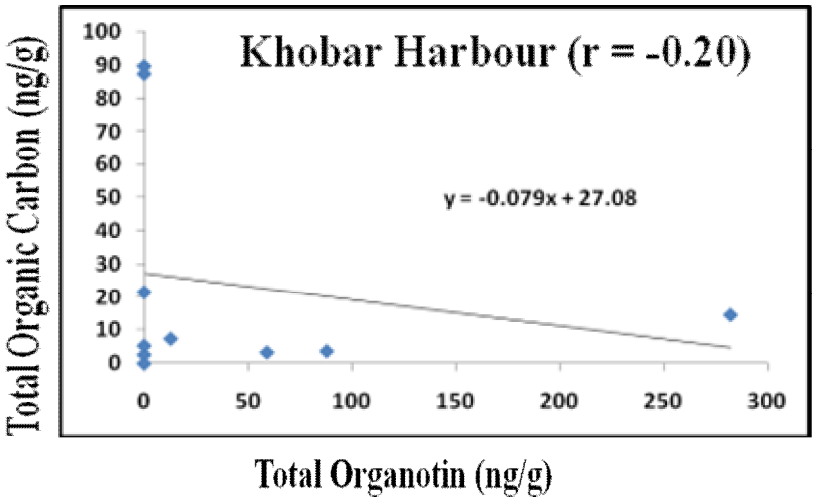


Figure 17: Relationship between DO and organotins in sediment





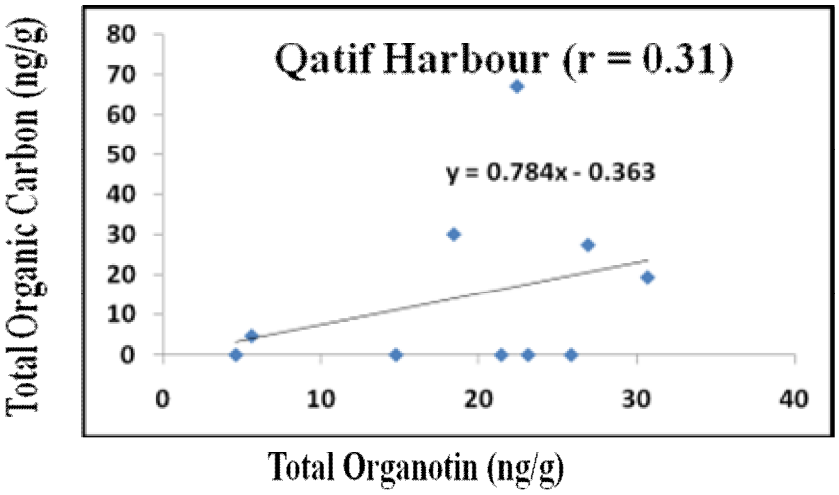


Figure 18: Relationship between TOC and organotins in sediment

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The concentrations of the six organotin species were studied in sediment and biota samples collected from different coastal stations. Generally, their concentrations were very low or below the detection limits. The organotins concentration in sediments samples from the Jubail harbour was much higher than in samples from Khobar and Qatif harbour. Some stations from the three locations exceeded the 5ng/g allowable limits set for sediment by the Australian environmental quality guidelines. Relatively high levels of organotins were observed close to the shoreline (0 – 250m) within the study area.

The observed organotin concentrations in the biota samples from Khobar and Qatif harbours were very low compared to the values from other parts of the world. The organotin levels showed increasing trend with increase in size of the bivalves collected from the study area.

The environmental parameters measured from the study area didn't show any significant influence on the concentration of organotins in sediment samples. While the values of some parameters remained unchanged for all the study area, others have varying values that do not have correlation to the concentration of organotins recorded.

5.2 Recommendations

a. It is required to monitor organotin levels in sediment and biota for developing baseline information for the western Arabian Gulf

b. It is necessary to develop environmental guidelines and standards for organotin level in sediment and biota samples from the Arabian Gulf

c. Regularly monitor organotin contaminants to assess persistence in the coastal environment.

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APPENDIX A

Location Coordinates of Sampling Locations

Table 9: Location Coordinates for Jubail Harbour Sampling

S/N	Station ID	Coordinates		Sampling Date
		X	Y	
1.	JB-01	27°0.678'N	49°40.853'E	01/03/2015
2.	JB-02	27°0.678'N	49°40.853'E	01/03/2015
3.	JB-03	27°0.678'N	49°40.853'E	01/03/2015
4.	JB-04	27°0.678'N	49°40.853'E	01/03/2015
5.	JB-05	27°0.678'N	49°40.853'E	01/03/2015
6.	JB-06	27°0.678'N	49°40.853'E	01/03/2015
7.	JB-07	27°0.678'N	49°40.853'E	01/03/2015
8.	JB-08	27°0.678'N	49°40.853'E	01/03/2015
9.	JB-09	27°0.678'N	49°40.853'E	01/03/2015
10.	JB-10	27°0.678'N	49°40.853'E	01/03/2015

Table 10: Location Coordinates for Qatif Harbour Sampling

S/N	Station ID	Coordinates		Date
		X	Y	
1.	QT-01	27° 32.629'N	50° 3.204'E	15/02/2015
2.	QT-02	27° 32.667'N	50° 2.170'E	15/02/2015
3.	QT-03	27° 32.761'N	50° 1.892'E	15/02/2015
4.	QT-04	27° 32.665'N	50° 1.919'E	15/02/2015
5.	QT-05	27° 32.619'N	50° 1.820'E	15/02/2015
6.	QT-06	27° 32.625'N	50° 1.742'E	15/02/2015
7.	QT-07	27° 32.659'N	50° 1.721'E	15/02/2015
8.	QT-08	27° 32.718'N	50° 1.705'E	15/02/2015
9.	QT-09	27° 32.765'N	50° 1.748'E	15/02/2015
10.	QT-10	27° 32.712'N	50° 1.845'E	15/02/2015

Table 11: Location Coordinates for Khobar Harbour Sampling

S/N	Station ID	Coordinates		Date
		X	Y	
1.	KB-01	26° 14.517'N	50° 13.481'E	20/03/2015
2.	KB-02	26° 14.409'N	50° 13.244'E	20/03/2015
3.	KB-03	26° 14.415'N	50° 13.280'E	20/03/2015
4.	KB-04	26° 14.422'N	50° 13.329'E	20/03/2015
5.	KB-05	26° 14.322'N	50° 13.224'E	20/03/2015
6.	KB-06	26° 14.319'N	50° 13.295'E	20/03/2015
7.	KB-07	26° 14.329'N	50° 13.345'E	20/03/2015
8.	KB-08	26° 14.295'N	50° 13.251'E	20/03/2015
9.	KB-09	26° 14.287'N	50° 13.317'E	20/03/2015
10.	KB-10	26° 14.259'N	50° 13.372'E	20/03/2015

Table 12: Location Coordinates for Half Moon Bay Sampling

S/N	Station ID	Coordinates		Date
		X	Y	
1.	KF-01	26° 54.443'N	50° 03.594'E	10/01/2015
2.	KF-02	26° 54.441'N	50° 03.191'E	10/01/2015
3.	KF-03	26° 54.362'N	50° 03.030'E	10/01/2015
4.	KF-04	26° 54.374'N	50° 02.895'E	10/01/2015
5.	KF-05	26° 54.436'N	50° 02.868'E	10/01/2015
6.	KF-06	26° 54.528'N	50° 02.838'E	10/01/2015
7.	KF-07	26° 54.610'N	50° 02.908'E	10/01/2015
8.	KF-08	26° 54.599'N	50° 02.974'E	10/01/2015
9.	KF-09	26° 54.377'N	50° 05.309'E	10/01/2015
10.	KF-10	26° 54.428'N	50° 02.923'E	10/01/2015

APPENDIX B

Organotins Concentrations in Sediments

Table 13: Concentration of Organotins in Sediment Samples from Jubail Harbour

JUBAIL	Organotin Compounds, ng/g						
Sample ID	**MBT**	**MPhT**	**DBT**	**DPhT**	**TBT**	**TPhT**	**TOTAL**
JB-01	144.4	320.4	87.57	411.64	-	-	**964.01**
JB-02	-	25	22.4	33.4	-	-	**80.80**
JB-03	344	654	36.8	58.5	-	-	**1093.30**
JB-04	-	-	28.9	41.8	-	-	**70.70**
JB-05	21.1	87	25.1	69.3	-	-	**202.50**
JB-06	-	-	125.58	670.8	-	-	**796.38**
JB-07	-	-	-	10.8	-	-	**10.80**
JB-08	-	-	-	51.1	-	-	**51.10**
JB-09	-	-	-	24.2	-	34.6	**58.80**
JB-10	-	-	-	16.4	-	-	**16.40**

Table 14: Concentration of organotins in Sediment Samples from Khobar Harbour

KHOBAR	organotin Compounds, ng/g						
Sample ID	**MBT**	**MPhT**	**DBT**	**DPhT**	**TBT**	**TPhT**	**TOTAL**
KB-01	21.9	59.7	6.38	-	-	-	87.98
KB-02	2.39	51.1	5.76	-	-	-	59.25
KB-03		9.2	3.62	-	-	-	12.82
KB-04	56.0	197	7.8	21.5	-	-	282.30
KB-05	-	-	-	-	-	-	0.00
KB-06	-	-	-	-	-	-	0.00
KB-07	-	-	-	-	-	-	0.00
KB-08	-	-	-	-	-	-	0.00
KB-09	-	-	-	-	-	-	0.00
KB-10	-	-	-	-	-	-	0.00

Table 15: Concentration of organotins in Sediment Samples from Qatif Harbour

QATIF	organotin Compounds, ng/g						
Sample ID	**MBT**	**MPhT**	**DBT**	**DPhT**	**TBT**	**TPhT**	**TOTAL**
QT-01	-	-	4.69	-	-	-	**4.69**
QT-02	6.09	58.2	2.70	-	-	-	**66.99**
QT-03	-	22.3	5.15	-	-	-	**27.45**
QT-04	-	24	6.1	-	-	-	**30.10**
QT-05	-	14.2	5.23	-	-	-	**19.43**
QT-06	-	-	-	-	-	-	**0.00**
QT-07	-	-	-	-	-	-	**0.00**
QT-08	-	-	-	-	-	-	**0.00**
QT-09	-	-	-	-	-	-	**0.00**
QT-10	-	-	-	-	-	-	**0.00**

Table 16: Concentration of organotins in Sediment Samples from Half Moon Bay

Half Moon BAY	organotin Compounds, ng/g						
Sample ID	**MBT**	**MPhT**	**DBT**	**DPhT**	**TBT**	**TPhT**	**TOTAL**
HB-01	-	-	2	-	-	-	**2.00**
HB-02	-	6	4	-	-	-	**10.00**
HB-03	-	2	-	-	-	-	**2.00**
HB-04	-	-	-	-	-	-	**0.00**
HB-05	-	-	5	-	-	-	**5.00**
HB-06	-	-	1	-	-	-	**1.00**
HB-07	-	-	-	-	-	-	**0.00**
HB-08	-	-	-	-	-	-	**0.00**
HB-09	-	-	-	-	-	-	**0.00**
HB-10	-	-	-	-	-	-	**0.00**

Table 17: Concentration of organotin in Standard Solutions

organotin Compounds		MBT	MPhT	DBT	DPhT	TBT	TPhT
Retention Time (min)	**AveRT**	4.71	7.75	8.16	11.03	13.46	17.77
Conc. Std. ng/ml	**ng**						
200	0.2000	271	263	584	948	617	520
500	0.5000	564	475	1178	1976	1287	1138
1000	1.0000	752	580	1518	2466	1699	1628
2000	2.0000	1735	1268	3422	5850	3966	3762
5000	5.0000	4139	2956	8152	14328	9674	9054
	Blank	4	-	3	1	1	6

Table 18: Calibration Parameters for Sediment Samples

Analytes	Slope	Intercept	R^2	LOD (ng/g)	LOQ (ng/g)	% Recovery
MBT	1269.1	422.4	0.994	1.0982	3.2946	94
MPhT	519.3	819.1	1.000	2.0927	6.2781	85
DBT	7052.2	1614.2	0.996	0.7553	2.2660	90
DPhT	3453.4	805.6	0.992	0.7698	2.3094	87
TBT	2485.7	848.7	0.991	1.1268	3.4145	82
TPhT	1709.5	213.2	0.992	0.4116	1.2473	80

APPENDIX C

Physico-Chemical Parameters of Sampling Locations

Table 19: Physico-Chemical Parameters for Jubail Harbour

Station ID	Temp. (°C)	pH	DO (mg/L)	Salinity
JB-01	22.9	7.42	3.13	45
JB-02	23.1	7.35	3.61	43
JB-03	23.2	7.37	4.12	39
JB-04	22.8	7.40	4.22	44
JB-05	23.4	7.41	4.23	37
JB-06	22.7	7.39	3.98	41
JB-07	22.6	7.35	3.78	40
JB-08	22.7	7.34	4.35	42
JB-09	22.9	7.35	3.69	38
JB-10	23.0	7.33	4.23	41

Table 20: Physico-Chemical Parameters for Qatif Harbour

Station ID	Temp. (°C)	pH	DO (mg/L)	Salinity
QT-01	21.0	7.98	4.31	38
QT-02	21.2	8.01	4.15	38
QT-03	20.9	7.81	5.22	37
QT-04	20.9	8.20	5.30	35
QT-05	20.8	8.33	6.11	33
QT-06	20.9	7.71	5.08	35
QT-07	20.7	7.80	4.78	35
QT-08	20.6	8.11	5.26	37
QT-09	20.8	7.66	4.84	36
QT-10	20.7	7.70	5.41	40

Table 21: Physico-Chemical Parameters for Khobar Harbour

Station ID	Temp. (°C)	pH	DO (mg/L)	Salinity
KB-01	23.1	7.55	4.13	49
KB-02	22.9	8.32	3.72	50
KB-03	22.7	8.24	5.67	48
KB-04	22.7	7.91	4.29	47
KB-05	23.1	8.31	3.63	45
KB-06	23.3	8.27	3.78	45
KB-07	23.1	7.93	3.72	48
KB-08	22.8	7.91	4.32	46
KB-09	22.9	8.20	3.89	44
KB-10	22.9	7.85	4.24	44

Table 22: Physico-Chemical Parameters for Half Moon Bay

Station ID	Temp. (°C)	pH	DO (mg/L)	Salinity
HB-01	21.6	6.98	6.97	36
HB-02	21.3	7.01	6.61	35
HB-03	21.7	7.20	7.12	39
HB-04	22.0	7.22	7.22	39
HB-05	22.4	7.31	7.23	38
HB-06	21.9	7.15	6.98	37
HB-07	21.3	7.26	6.78	36
HB-08	21.8	6.87	7.35	36
HB-09	22.1	7.33	6.69	37
HB-10	21.2	7.52	7.23	35

APPENDIX D

Total Organic Carbon in Sampling Locations

Table 23: Concentrations of Total Organic carbon in Sediments from Jubail Harbour

SAMPLE CODE	WEIGHT(mg)	CONC. (ng/g)
JB-1	208.6	33.14
JB-2	201.3	11.22
JB-3	202.8	9.98
JB-4	203.3	11.29
JB-5	200.2	12.29
JB-6	201.1	25.29
JB-7	200.5	8.63
JB-8	200.3	7.87
JB-9	202.0	9.09
JB-10	202.8	12.30

Table 24: Concentrations of Total Organic carbon in Sediments from Qatif Harbour

SAMPLE CODE	WEIGHT(mg)	CONC. (ng/g)
QT-01	204.2	5.64
QT-02	200.3	22.45
QT-03	203.3	26.94
QT-04	205.5	18.44
QT-05	204.8	30.71
QT-06	202.9	4.64
QT-07	205.5	21.45
QT-08	200.0	23.15
QT-09	201.1	14.78
QT-10	202.5	25.87

Table 25: Concentrations of Total Organic carbon in Sediments from Khobar Harbour

SAMPLE CODE	WEIGHT(mg)	CONC. (ng/g)
KB-01	204.4	3.72
KB-02	205.2	3.34
KB-03	201.5	7.43
KB-04	205.8	14.65
KB-05	203.3	89.72
KB-06	201.9	87.42
KB-07	200.6	2.64
KB-08	203.9	5.34
KB-09	203.9	21.53
KB-10	202.5	0.01

Table 26: Concentrations of Total Organic carbon in Sediment from Half Moon Bay

SAMPLE CODE	WEIGHT(mg)	CONC. (ng/g)
HB-01	202.7	0.00
HB-02	201.7	0.99
HB-03	200.1	0.97
HB-04	200.5	0.48
HB-05	200.7	0.49
HB-06	203.4	0.82
HB-07	203.3	0.03
HB-08	204.5	0.62
HB-09	200.1	0.60
HB-10	203.4	0.00

APPENDIX E

Grain Size Analysis

Table 27: Summary of grain size distribution and sediment description

Sampling Stations	MEAN (μm)	MEAN (ϕ)	SORTING	SKEWNESS	KURTOSIS	SEDIMENT DESCRIPTION
JB-01	15.54	6.01	2.56	-0.01	0.76	Slightly Very Fine Gravelly Medium Silt
JB-02	15.05	6.05	2.80	-0.06	0.85	Slightly Very Fine Gravelly Very Coarse Silt
JB-03	14.52	6.11	3.58	0.07	1.17	Slightly Very Fine Gravelly Very Coarse Silt
JB-04	2.07	8.92	1.56	0.00	0.74	Slightly Very Fine Gravelly Mud
JB-05	2.12	8.88	2.77	0.37	2.74	Slightly Very Fine Gravelly Mud
KB-01	452.74	1.14	2.41	0.25	0.95	Very Fine Gravelly Medium Sand
KB-02	229.75	2.12	2.40	0.30	1.28	Slightly Very Fine Gravelly Fine Sand
KB-03	11.19	6.48	9.408	0.644	0.806	Slightly Very Fine Gravelly Medium Sandy Mud
KB-04	14.03	6.16	12.04	0.694	0.551	Slightly Very Fine Gravelly Coarse Sandy Mud
KB-05	4.459	7.81	3.468	0.459	0.873	Slightly Very Fine Gravelly Very Fine Silt

Table 28: Summary of grain size distribution and sediment description

Sampling Stations	MEAN (μm)	MEAN (ϕ)	SORTING	SKEWNESS	KURTOSIS	SEDIMENT DESCRIPTION
KF-01	175.6	2.510	1.642	-0.031	1.351	Slightly Very Fine Gravelly Fine Sand
KF-02	255.3	1.970	1.781	-0.391	0.983	Slightly Very Fine Gravelly Medium Sand
KF-03	259.2	1.948	1.743	-0.374	0.993	Moderately Sorted Medium Sand
KF-04	186.1	2.426	1.803	-0.038	1.050	Moderately Sorted Fine Sand
KF-05	87.70	3.511	17.85	-0.204	0.608	Very Fine Gravelly Muddy Very Fine Sand
QT-01	14.61	6.097	2.591	-0.046	0.812	Slightly Very Fine Gravelly Very Coarse Silt
QT-02	14.41	6.116	2.655	-0.060	0.839	Slightly Very Fine Gravelly Very Coarse Silt
QT-03	14.68	6.090	2.478	-0.017	0.764	Slightly Very Fine Gravelly Medium Silt
QT-04	14.82	6.077	2.437	0.000	0.738	Slightly Very Fine Gravelly Medium Silt
QT-05	15.55	6.006	2.914	0.016	0.924	Slightly Very Fine Gravelly Very Coarse Silt

APPENDIX F

Length and Weight of Biota

Table 29: Length and Weight of Biota from Khobar Harbour

S/N	Code	Length (mm)	Total Weight (g)	Wet Tissue Weight (g)	Dry Tissue Weight (g)
1.	AZ-1	57.01	102.1	15.82	30.03
2.		59.62	101.2	11.72	
3.		56.33	81.93	13.04	
4.		54.94	86.28	13.75	
5.	AZ-2	56.77	91.23	15.43	14.41
6.		56.65	87.44	15.24	
7.		55.48	84.43	17.28	
8.		51.35	67.34	10.64	
9.		52.21	59.94	7.54	
10.	AZ-3	37.33	25.90	5.36	2.84
11.		32.27	19.95	2.73	
12.		30.05	17.14	2.38	
13.		31.54	20.12	3.37	

Table 30: Length and Weight of Biota from Qatif Harbour

S/N	Code	Length (mm)	Total Weight (g)	Wet Tissue Weight (g)	Dry Tissue Weight (g)
1.	BZ-1	61.28	139.41	15.19	18.95
2.		68.74	133.74	8.74	
3.		57.17	160.00	16.34	
4.		67.95	143.97	12.97	
5.		63.35	172.97	15.74	
6.	BZ-2	65.01	195..67	17.77	24.29
7.		74.01	174.22	20.80	
8.		70.36	180.12	13.44	
9.		73.77	232.86	15.63	
10.		75.23	169.19	16.62	
11.	BZ-3	117.85	469.51	42.08	42.55
12.		100.06	424.96	35.77	
13.		98.90	293.26	27.96	
14.		78.95	258.37	16.31	
15.		98.07	301.35	25.68	

APPENDIX G

Survey Questionnaire

Earth Science Department
King Fahd University of Petroleum and Minerals

Marine Environmental Monitoring

Location:_____ Date:_____ Time:_____

1. **What kinds of crafts are moored here? _____**
2. **How long do they stay in dock? _____**
3. **Is any ship repair activity done here? _____**
   If no, where is it done? _____
4. **What type of repair activity is done here? _____**
5. **What types of craft are repaired here? _____**
6. **How often is the repair activity done? _____**
7. **Is any ship painting activity done here? _____**
   If no, where is it done? _____
8. **How often is the painting done? _____**
9. **What kinds of paints are used? _____ Paint brand name_____**
10. **What types of craft are painted here? _____**

APPENDIX H

Figure 19: Sediment sample collection using Van Veen Grab

Figure 20: Hand picking of Clams at low tide

Figure 21: A scuba diver ready to dive for collecting Oysters

Figure 22: Half Moon-16, the research vessel used for sampling

Figure 23: Ship painting caught on site at Jubail Harbour

Figure 24: Collection of Antifouling paint samples for analysis

Figure 25: Wet sediment samples being air dried

Figure 26: Sediment samples after drying and sieving

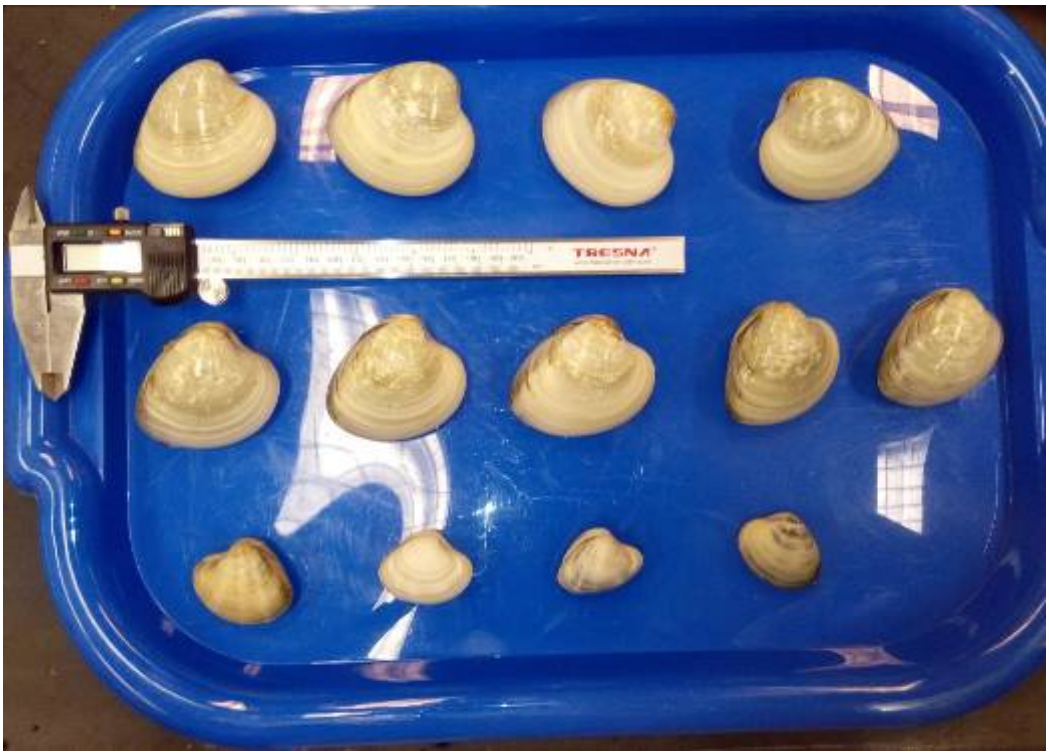

Figure 27: Biota samples (Clam) - *Meretrix meretrix*

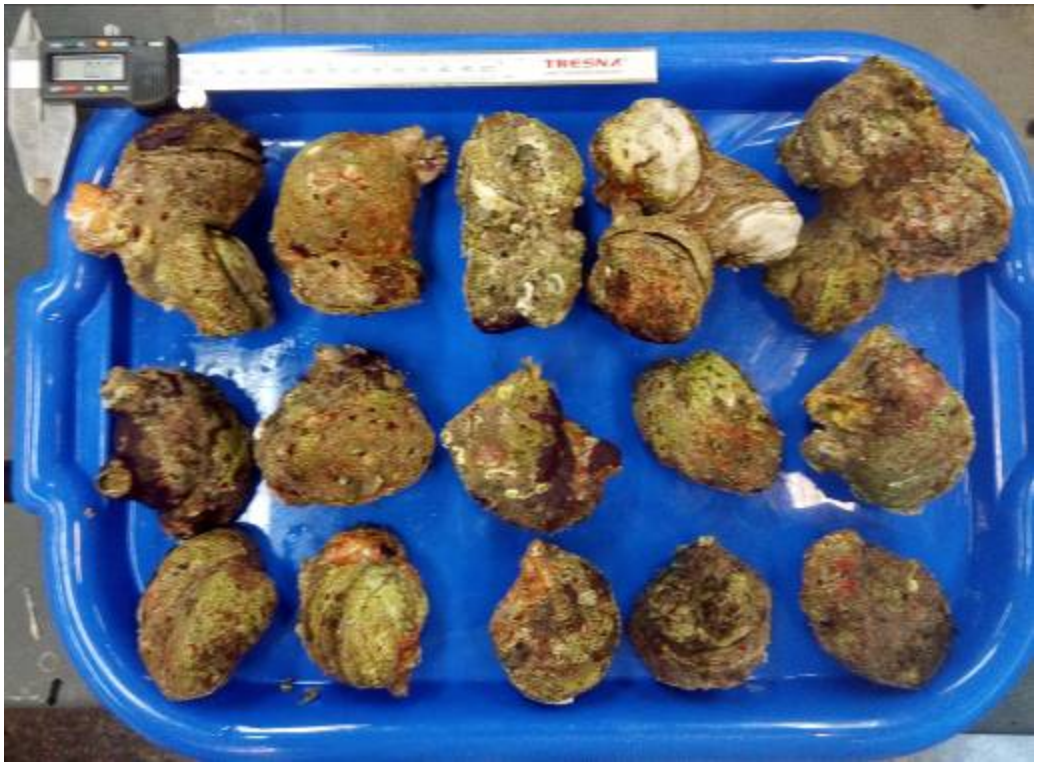

Figure 28: Biota samples (Oyster) - *Chama species*

Figure 29: The Agilent GC-MS Machine used for the analysis

Figure 30: Laconco Freeze drying equipment (left) and Shimadzu TO Analyzer (right)

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